DTU Library

Environmental life cycle assessments of producing maize, grass-clover, ryegrass and winter wheat straw for biorefinery

Parajuli, Ranjan; Kristensen, Ib Sillebak; Knudsen, Marie Trydeman; Mogensen, Lisbeth; Corona, Andrea; Birkved, Morten; Peña, Nancy; Graversgaard, Morten; Dalgaard, Tommy

Published in:
Journal of Cleaner Production

Link to article, DOI:
10.1016/j.jclepro.2016.10.076

Publication date:
2017

Document Version
Peer reviewed version

Environmental life cycle assessments of producing maize, grass-clover, ryegrass and winter wheat straw for biorefinery

Ranjan Parajuli[a,*1], Ib Sillebak Kristensen[a], Marie Trydeman Knudsen[a], Lisbeth Mogensen[a], Andrea Corona[b], Morten Birkved[b], Nancy Peña[c], Morten Graversgaard[a], Tommy Dalgaard[a]

[a]Department of Agroecology, Aarhus University, Blichers Allé 20, 8830-DK Tjele, Denmark

[b]Department of Management Engineering, Technical University of Denmark, Building 424, DK-2800 Lyngby, Denmark

[c] Institute of Environmental Science and Technology, Autonomous University of Barcelona, Carrer de les Columnes-08193 Bellaterra, Barcelona, Spain

[*]Corresponding author, email: ranjan.parajuli@agro.au.dk, Phone: +4571606831

Abstract:

The aim of this study is to assess the potential environmental impacts of producing maize, grass-clover, ryegrass, and straw from winter wheat as biomass feedstocks for biorefinery. The Life Cycle Assessment (LCA) method included the following impact categories: Global Warming Potential (GWP_{100}), Eutrophication Potential (EP), Non-Renewable Energy use (NRE), Potential Fresh Water Ecotoxicity (PFWTox) and Potential Biodiversity Damages (PBD). The results showed that GWP_{100} (in kg CO_2 eq, including contribution from soil carbon change) for producing 1 ton of dry matter (t DM) was highest for ryegrass, grass-clover and maize, and lowest for straw. The carbon footprints of ryegrass, grass-clover and maize were affected by including the contribution from soil organic carbon (SOC) changes. Nitrous oxide emissions and emissions related to the production of agro-chemicals (including N-fertilizer) were other hotspots in the carbon footprint. The EP calculated per t DM was highest for grass-clover, ryegrass and maize, and was lowest for straw. NRE use (MJ eq/t DM) was highest for ryegrass, grass-clover and maize and lowest for straw. Major hotspots were diesel use for field operations and agro-chemicals production. The PBD, expressed as Potentially Disappeared Fraction (PDF) showed the highest adverse impact to biodiversity in maize, followed by straw, whereas the results showed relatively lower impact for ryegrass and grass-clover. The PFWTox (CTU_e/t DM), at farm level was highest for straw, followed by maize, whereas the values were significantly lower for grass-clover and ryegrass. These variations in ranking of the different biomasses productions using different impact categories for environmental performance showed that it is important to consider a wider range of impact categories for assessing environmental sustainability.

Keywords: Life Cycle Assessment, biorefinery, environmental impacts, ecotoxicity, soil organic carbon, Denmark

---

[1] Corresponding author: parajuliranjan@gmail.com

1. Introduction

The current sustainability goals in the European Union (EU) are targeted to address energy insecurity concerns and emphasized on the promotion of a green growth economy through implementation of different measures including displacement of fossil fuels and establishment of a strong biobased economy (Nebe, 2011). The European Biorefinery Vision and Roadmap for 2030 (Kircher, 2012) clearly stressed on the importance of diversifying biomass production and development of biorefineries. Biomass is one of the principal input to biorefineries, hence environmental sustainability assessment of producing them are relevant for long term sustainability (Parajuli et al., 2015; Ragauskas et al., 2006).

Life Cycle Assessment (LCA) is an analytical tool to calculate the potential environmental impacts of a production system (Rebitzer et al., 2004), and is one of the best available tools used in EU for different production sectors including agriculture (European Commission, 2015). Few LCA studies have compared the environmental impacts of producing several biomass feedstocks, and most of them focused on the greenhouse gas (GHG) balances. Mogensen et al. (2014) made a comparison of different types of crops, however with a focus on carbon footprint. Vellinga et al. (2013) compared the environmental performance of fresh grass, grass silage and maize (silage), but focussed mainly on Global Warming Potential (GWP), and assumed constant rate of Soil Organic Carbon (SOC) change. In general, changes in SOC mainly depend on the land use change history (Guo and Gifford, 2002). Furthermore, few LCA studies have integrated the partial carbon budget for individual crops and combined these budgets with the biomass decay process, which changes with time perspectives on the release of CO2 from soil to the atmosphere (Petersen et al., 2013). These aspects are important to assess the importance of soil carbon cycling to the overall environmental impacts (e.g. GWP and aquatic eutrophication) (Powlson et al., 2011). Furthermore, it is also important to evaluate management options e.g. to analyse soil carbon sequestration possibilities while developing large scale biofuel production systems (Schmidt et al., 2011) and other high value renewable products (Parajuli et al., 2015). Furthermore, additional concerns, related to the effects of agro-chemicals (e.g., pesticides) released to the environment, land use change effects (direct and indirect) and potential biodiversity damages are relevant to be analysed when biomasses are to be screened for different conversion pathways.

The aim of the present study was to include several impact categories for evaluating the environmental burdens of producing different biomass types representing Danish and similar type of agro-climatic condition. It included contribution from soil organic matter through use of C-tool (Petersen et al., 2013). Risks of pesticides leaching and eutrophication impact to the freshwater ecosystem are also included in the study. In general, in most of the LCA studies, while assessing impacts of pesticides, emission distributions of the active ingredients (a.is) to air and freshwater (Birkved and Hauschild, 2006) were often not considered, and/or those if however included the effect of the local climatic parameters to the distributions were not considered. This study covered the emission distribution of pesticides to freshwater and air in a specific agro-climatic conditions and pesticides application scenarios (Dijkman et al., 2012).

2. Materials and Methods

2.1. System boundary and functional unit

The agricultural biomass production systems studied in this paper are: Maize, grass-clover, ryegrass and straw from winter wheat. Grass-clover and ryegrass are perennial crops grown in crop rotation, while others are annual crops. The defined system boundary for the biomass production is illustrated in Figure 1. The functional unit (FU) of the assessment is 1 t dry matter (DM) of the respective biomass types. In addition, the results are also expressed per hectare (ha) and per Mega Joule (MJ) of the harvested biomasses.

Figure 1: The farm gate system boundary defined for the biomass production.

2.2. Environmental impact categories and assessment methods

The environmental impact categories are: Global Warming Potential-100 (GWP_{100}) (with and without contribution from SOC changes), Eutrophication Potential (EP), Non-Renewable Energy (NRE) use, Potential Freshwater Ecotoxicity (PFWTox) and Potential Biodiversity Damage (PBD). The “EPD 2013” and “EPD 2008” method (Environdec, 2015) were used to calculate the first three impact categories. The PFWTox was calculated by covering the indirect emissions at the background processes (section 2.3) and emissions from the active ingredients (a.is) while applying to the field. For the foreground processes, the impact was calculated using the ILCD method (European Commission, 2012a). With regard to the applied pesticides, at the farm level PFWTox was calculated by using PestLCI 2.0.6 (Dijkman et al., 2012) and USEtox (Rosenbaum et al., 2008) models (section 2.4.4). The background and foreground toxicological measures were added to calculate the total PFWTox. The LCA modeling was done by using the PC tool “SimaPRO 8.0.4” (PRé Consultants, 2015). Regarding the PBD, it was based on the loss of plants species richness and was calculated by using characterisation factors (CFs), in accordance to Knudsen et al. (2016). It should be noted that in the case of straw, the environmental impact potentials were divided between wheat and wheat straw using economic allocation. The allocation factor was 19% to straw based on prices for sales of straw and cereals for the period 2011-2015 (SEGES, 2015a).

2.3. Data source for the background and foreground processes

The system boundary was constituted of: (i) the background system, (upstream side processes) and (ii) the foreground system (downstream side processes). The background processes included the product system of material inputs (e.g. fuel, chemicals, and agro-machineries) and their supply to the foreground processes. All the necessary data related to the background system were based on Ecoinvent 3 (Weidema et al., 2013), unless otherwise stated in the text.

The foreground system included the central activities related to the biomass production (Figure 1). Necessary material inputs (Table 1) and assumptions for the related emissions at the foreground level are described in Table 2-4. Yield of maize, grass-clover and ryegrass were based on average Danish farm yields (2007-2011) (Kristensen, 2015; Statistics Denmark, 2013) and for the winter wheat grain (Oksen, 2012; Statistics Denmark, 2013) (Table 1). Straw represents 55% of the net cereal yield (Taghizadeh-Toosi et al., 2014).The synthetic fertilizer (N=Nitrogen, P= Phosphorous, K= Potassium) inputs are based on the current Danish regulation for nutrient application (NaturErhvervstyrelsen, 2015) (Table 1). The assumed synthetic fertilizers are: N=calcium ammonium nitrate (CAN) (NPK 26.5 at plant/RER/Economic), P= triple superphosphate (RER/Alloc Def, U) and K= potassium chloride (RER/Alloc Def, U). CFs for the emissions related to fertilizers were based on Agri-footprint (2014) and Ecoinvent v3 (Weidema et al., 2013). Types of pesticides and mass of active ingredients (a.is.) were based on Ørum and Samsøe-Petersen (2014) and a detailed description of this can be found in the Supporting Information (SI).

2.4. Life cycle inventory

2.4.1. Crop production system

In this study, the selected crops are assumed to be grown on Danish arable farm with sandy soils, i.e. the soil type JB1-JB4 (NaturErhvervstyrelsen, 2015); where the clay content (< 2 µm particles) is less than 10%. The crops that are most commonly grown in the Danish arable land includes: cereals and fodder crops (e.g. temporary grass) accounting for 55% and 21% respectively of the Danish agricultural area (European Commission, 2012b).

The production cycles for maize and winter wheat are assumed to be 1 year-cycle, and for grass-clover and ryegrass are assumed 2 years (Jørgensen et al., 2011). Frequencies of fertilizer application for the crops were: maize (2 times/year), grass-clover and ryegrass (3 times/year) and winter wheat (2 times/year/ha). Likewise, frequency of pesticides spraying were: maize (2 times/year/ha), winter wheat (3 times/year) and for grass-clover and ryegrass were 2 times/year/ha (Jørgensen et al., 2011). The harvest frequency for grass-clover and ryegrass were four cuts in a year (Jørgensen et al., 2011). Diesel consumption for the farm operations was based on Dalgaard et al. (2001). Heating value and density of diesel in the current study are 35.95 MJ/l and 0.84 kg/l respectively (Weidema et al., 2013). The total primary energy input (in MJ/ha/y) for the selected crops are shown in Table 1. With regard to the production of winter wheat energy input for drying grain was included and set to 6.8

MJ (electricity) and 6.2 MJ_{heat} (heat, input as oil) per 100 kg of cereals respectively (Kristensen and Grundtoft, 2003).

Table 1: Input-output for the crop production, per ha per year

2.4.2. Calculation of soil carbon changes

The C-tool model (Petersen et al., 2013) was used to simulate the soil organic carbon (SOC) turnover. With the set of parameters related to the C assimilation from residues and soil (Taghizadeh-Toosi et al., 2014) the model can evaluate effects of agricultural management options on SOC storage in temperate agricultural soils. In the current study, the initial SOC stock was assumed as 90 t C/ha (to the soil depth of 0-100 cm) and the carbon inputs from the plant residues are shown in Table 2. Details on the methods to run the model are described in Taghizadeh-Toosi et al. (2014). The SOC turnover was calculated as the differences between carbon input available from the reference land use and the current land use. Spring barley production (with 100% straw incorporated to soil) was assumed as the reference land use case (Table 2). The contribution from SOC change is calculated in a 100 year perspective according to Petersen et al. (2013) assuming a sequestration of 9.7% of C input.

Table 2: Carbon sequestration as a result of soil C changes between the reference land use and the production of the selected crops

2.4.3. Calculation of N and P emissions

A field N balance method was used to calculate N-leaching, after accounting for all the N-related inputs and outputs (Table 4). Direct and indirect nitrous-oxide emission (N_2O-N) were based on emissions factors reported in IPCC (2006). Factors assumed for NH_3 emission from: N-fertilizer were based on reports (EEA, 2013; Nemecek and Kägi, 2007) and from the crops (Sommer et al., 2004). Denitrification was calculated using SimDen model (Vinther, 2005). All the related basic assumptions are shown in Table 3. The Soil Organic Nitrogen (SON) change was calculated using the C-tool model (Taghizadeh-Toosi et al., 2014) and assuming 20 years cultivation with the same assumed yields and corresponding plant residues (Table 4).

Table 3: Emission factors used in the study

Table 4: N balances and emissions, per 1 ha of the crop production

2.4.4. Emissions related to pesticide application at farm level

Emission distributions of active ingredients (a.is) to air (f_a), surface water (f_{sw}), ground water (f_{gw}) and the fraction being taken up by the plants (f_{uptake}) (Birkved and Hauschild, 2006) were calculated by using the model PestLCI 2.0.6 (see SI Table S3-Table S5). For those a.is not included in the PestLCI2.0.6, related mixing partners of the a.is (i.e. generally mixed while spraying) were chosen from the database (SEGES, 2015b) and by using expert judgements. For such a.is, average emission distribution fractions were calculated from the emissions simulated in different field scenarios (see SI, Table S2). The potential freshwater ecotoxicity (PFWTox) (Hauschild et al., 2013) was calculated by multiplying the emission distribution fractions (to air and surface water) with the respective comparative ecotoxicity units (expressed as CTU_e per kg of emission) simulated by using USEtox model. The method was in accordance with Fantke et al. (2015) and Nordborg et al. (2014).

2.4.5. Biodiversity changes

The Potential Biodiversity Damage (PBD) was based on the loss of plant “species richness” and the approach, as suggested in De Schryver et al. (2010). The characterization factor (in PDF) used in this study were for: maize and winter wheat (0.68), grass-clover (0.09) and ryegrass (0.12), and represented conventional (intensive) farming (Knudsen et al., 2016).

3. Results and discussion

3.1. Life Cycle Inventory analysis

The primary energy input per ha for the farm operations calculated in this study was close to the values reported in Mogensen et al. (2014), and the minor differences were partly because of differences in the assumed parameters, e.g. heat value of diesel was assumed as 36.4 MJ/l (Weidema et al., 2013) and fuel consumption for transporting biomass within the farm was separately shown as ton kilometre (t km) in this study, whilst was included in the energy consumed for the field work in their study.

Upon the comparison among the selected biomass types considered in the current study, the primary energy input was found to be highest for producing maize, followed by grass-clover, ryegrass and straw (Table 1). It was partly related to diesel input for the tillage activities, which was higher for maize and winter wheat production. Likewise, the harvesting process for maize crop had energy input of 1891 MJ/ha/y and was higher than winter wheat. Moreover, the frequency of harvesting and handling of grass-clover and ryegrass with high moisture content was the reason for higher primary energy input among the selected biomasses (Table 1). Apart from this, straw accounted energy input for baling (assumptions are shown in the footnotes of Table 1). Likewise, both grass-clover and ryegrass were baled after harvest, and the primary energy input for harvesting was also higher for them (Table 1).

Upon the analysis on the SOC changes, maize had a loss of 114 kg C/ha/y. In contrast, the SOC changes for grass-clover, ryegrass and straw showed tendency of mitigating GHG emission, which was -266, -340 and -16 kg C/ha/y for respectively. However, the SOC change is dependent on organic matter turnover in the soil and other agro-climatic conditions that influences the turnover (Benbi et al., 2014).

N-leaching was calculated by using the N balance method, which depends on the system boundaries and the N-flows, e.g. input-output of N and whether the internal flows are taken into account in the assessment (Watson et al., 2002). The calculation for N-leaching accounted all the forms of N-inputs (including the deduction of N-fixation for grass-clover mixture from the total N-input norms) and the internal flows (e.g. N emissions) and soil N changes. This study, focused on a single crop, but included the nitrogen left over after ryegrass and grass-clover (81 kg N/ha) as reduced fertilization application of the 2 year old grasses. The soil organic N availability for plant growth is also affected by the plant litter inputs maintaining the SOC stock despite of more decomposition (Philben et al., 2016). This was also reflected in our study, e.g. soil N mining was found in the case of maize production (-17 kg N/ha/y) with lower residues available to soil, and was opposite for the rest of the biomasses (Table 4). Of the total nitrous oxide ($N_2O_{direct+indirect}$) emissions, the direct emissions was in the range of 79%-97%, primarily related to the emissions from the applied fertilizer. The highest range was represented by the production of ryegrass and the lowest by winter wheat. NH_3 emission was highest with ryegrass, and was found mainly associated with the volatilization from the applied fertilizer (i.e. 92% of the total NH_3 emission) It was 59% in the case of maize, whereas was 89% and 59% of total NH_3 emission (Table 4).

3.2. Environmental impacts

The net GHG emission calculated per ha of the biomass production was highest for ryegrass and was followed by maize, grass-clover and straw (Table 5). The impact per t DM was lowest for straw and highest for ryegrass (Figure 2). Soil carbon sequestration was highest for ryegrass and grass-clover, which had positive impact on mitigating the GHG emission (Table 5). In contrast there was a debit of carbon emissions in the case of maize (Table 2). A similar order was found for the impact assessed per energy content (MJ) of the selected biomasses (Table 6).

Eutrophication potential calculated per t DM of biomasses was highest for grass-clover, ryegrass and maize (Table 5 and Figure 2). With regard to NRE use calculated per t DM, it was highest for ryegrass, grass-clover and maize (Figure 2). The results were connected with the ratio of N-fertilizer utilization efficiency and the primary energy input depending on the frequency of farm operations that are carried out throughout the production cycle of the biomasses (Table 2). Similar order was found for the impact calculated per MJ of the harvested biomasses.

With regard to the biodiversity impact, the negative impact was highest for maize and straw (Figure 2). The result showed lower impact on biodiversity for ryegrass and grass-clover compared to producing maize and straw.

Finally, the PFWTox related to the pesticides applied at farm level was highest for straw compared to rest of the biomasses (Table 5 and 2.b). The reasons behind having a higher PFWTox in the case of producing winter wheat crop and hence for straw was partly because of a higher amount of pesticides applied to the crop and the types of active ingredients used. In addition, the total PFWTox, i.e. including both the emissions at the background and foreground systems are shown in Table 5. The total ecotoxicity was related to emissions of toxic chemicals during the production of the material inputs going to the farm system.

Table 5: Environmental impact potentials for the production of the selected biomasses, per 1 ha

Table 6: Environmental impact potentials of the selected biomass feedstocks per t DM and per MJ

Figure 2: Environmental impact potentials of producing the selected biomass types (GWP_{100} includes soil C change).

3.3. Environmental hotspot assessments

3.3.1. Global Warming Potential

It was found that about 36%-46% of the gross GWP_{100} was a result of N_2O emissions. The gross impact denotes the impact potential without SOC change. This is in line with Mogensen et al. (2014), Knudsen et al. (2014) and Kramer et al. (1999). The impact however can be lowered by about 40-50% with a low N input system compared to a high N- input system Hauggaard-Nielsen et al. (2016) suggested that the treatment of legume pure stand had about 25-50% of the GHG emissions of the pure-stand grasses, depending on the level of N-inputs. In our study the legume-grass mixture (grass-clover) amounted 76% of the net GHG emissions of the purestand ryegrass (i.e. lowered by around 24%) (Table 5). The contribution from N-leaching to the total N_2O emissions was however not significantly influencing the total GHG emissions, at least compared to the direct N_2O emissions (section 3.1). Hauggaard-Nielsen et al. (2016) reported that with a 50% higher or lower level of N-leaching would have an impact of varying the carbon footprint by only 2-5%.

The production of agro-chemicals contributed in the range of 38% to 49% of the gross impact calculated for producing the biomasses. Significant amounts of N_2O are emitted during the production of nitric acid, which is part of ammonium nitrate production, and was another reason for contributing for a higher impact, which was also checked after Agri-footprint (2014). However it can be mitigated technically, e.g. by the choices of different N-fertilizer types (Brentrup et al., 2004). The tendency of such is discussed in section 3.5.3.

The contribution from the field operations (tillage + application of agro-chemicals + harvesting and loading) ranged from 6%-15% of the gross impact (Figure 3.a). In particular, the contribution from the diesel input to produce 1 t DM of ryegrass and maize was higher for the process "harvesting and loading". It covered 6% and 5% of the respective gross GWP_{100}. Furthermore, in the stated contribution, indirect emissions from the machine used in the farm are not included. Transportation activities contributed in the range of 3-4% of the gross GWP_{100} for the selected crops (Figure 3).

3.3.2. Eutrophication Potential

Nitrate, ammonia and phosphate emissions jointly contributed with 53%-64% of the total EP for the selected biomasses (Figure 3.b). The EP was as a result of N-leaching and further compounded by NH_3 emissions (see Table 4). It should be noted that EP for ryegrass ranked higher than maize (Table 5 and Figure 2), despite the N-leaching from the crop was the lowest. The reason behind this was that the characterization factors to the EP are higher for NH_3, and N_2O than nitrate emissions (Environdec, 2015). These emissions were higher in the ryegrass compared to the other crops (Table 4). Furthermore, it should also be taken into account that N-leaching generally depend on a number of parameters, e.g. temperature, precipitation, seasons, methods of fertilizer application, crop rotation history and changes in soil N; hence uncertainties exist. For instance, under different agro-climatic conditions nitrate leaching for maize was reported between 10-214 kg N/ha/y (Manevski et al., 2015); for grass-clover it was 4-21 kg N/ha for (Eriksen et al., 2004); and for winter wheat between 42-75 kg N/ha (Elsgaard et al., 2010; Thomsen et al., 1993). Furthermore, generally, perennial ley farming is associated to a lower risk of nitrate leaching; however, it is dependent on the period of incorporating the fertilizer. For instance, Tidåker et al. (2014) reported that if the incorporation is made during the summer or early autumn before sowing the winter wheat ((a case of Swedish crop rotation) (Larsson et al., 2005)), more N would be leached compared to the late autumn or early spring (before sowing of spring barley). In addition to this, it was further stressed that a higher proportion of clover in the grass-clover mixture could further signify the importance of the timing of incorporating the fertilizer, and hence thus the resulting a reduction in eutrophication potential and the GHG emissions, in particular by lowering the amount of N-fertilizer. Improvements in agricultural management practices (Martinez-Alier et al., 1998) can control the nitrate leaching and thus also control the eutrophying potential to the aquatic environment (Kirchmann et al., 2002; McLenaghen et al., 1996). For example, introduction of winter "catch crops" can control nitrate leaching (Martinez-Alier et al., 1998), however the assessment should consider the potential changes in nitrogen dynamics in cropping system that may lead to change in nitrogen losses. Catch crops inclusion in a crop rotation is regarded as a management tool, because of which the prolonged soil cover and effective soil N uptake are argued to check the potential N-leaching (Thorup-Kristensen et al., 2003), which otherwise would be high especially in sandy soil and in the situation if the soil is left uncropped (Simmelsgaard, 1998) These tendencies of soil nutrient management in a crop rotation cycle was limited in our study, especially tracking them in the N-balanced method. Furthermore, achieving a higher land use efficiency and at the same time lowering the NO_3 leaching rates are among the ways to lower aquatic eutrophication potential (Brentrup et al., 2004). To correlate the rate at which the eutrophication potential may vary because of changes in the N-leaching is 0.1 kg PO_4eq per kg of the nitrate emission (Environdec, 2015).

In addition to the stated EP calculated for the selected biomasses, the production of agro-chemicals, and mainly N-fertilizer contributed with 20%-43% of the total EP (Figure 3.b); the absolute values however were not modest (Table 5 and Figure 2).

3.3.3. Non-Renewable Energy use

The NRE use, related to diesel fuel consumption for maize, grass-clover, ryegrass and winter wheat was in the range of 17%-33% (Table 5). This was primarily related to the field operation processes. The lowest share was for grass-clover and ryegrass, which was partly because of the fact that on an annual basis these biomasses required less mechanical operations (e.g. only sowing) compared to other crops. Furthermore, the harvesting and loading covered 12% of the total NRE use for maize, which was followed by 16% for grass-clover, 13% for ryegrass and 8% for winter wheat. Furthermore, agro-chemical production covered in the range of 56%-75% of the NRE use (Figure 3.c). Transportation activities contributed with 8%-11% of NRE use. The contribution from the seed production was lower; however, for winter wheat it contributed with 5% of the NRE use respectively (Table 5 and Figure 3.c).

3.3.4. Other impact categories

With regard to the impact of applying pesticides at the farm level, the calculated PFWTox score for straw produced from winter wheat was 1.06 CTU_e/ t DM. PFWTox in the case of maize was lower compared to straw (Figure 3). Likewise, in the case of grass-clover and ryegrass it was lower by a 53-fold (Figure 2). However, crop-wise comparison showed that winter wheat production had the highest PFWTox (Figure 2). The reason behind the case of having the highest impact score in the case of winter wheat was related to higher emission distribution to air and freshwater per kg of applied active ingredients, particularly from the pesticides such as fluroxpyr, pendimethalin, epoxiconazole and pyraclostrobin. The characterization factors were also higher for these active ingredients (see supporting document-S3). Most importantly the total doze applied per ha in the case of winter wheat is 6.12 kg a.is/ha/y. Likewise, the characterization factors of the other pesticides used in the case of other biomasses were found relatively lower. Regarding the total PFWTox, the major contribution was 13% from the emissions at the farm level, and rest was related to foreground processes and indirect emissions from the operation of farm utilities, e.g. 32% of the total

PFWTox in the case of winter wheat was related to seeds production and 15% was related to electricity production that was supplied for drying grains. In contrast emissions of pesticides at the farm level for grass-clover and ryegrass had a contribution of merely 0.03% of the total PFWTox, seed production contributed about 4%, and rest was related to the indirect emissions from the production and operations of farm utilities. In the case of maize seed production contributed 16% of the total PFWTox and emission from the applied pesticides contributed 0.8%.

Figure 3: Environmental impact potentials in the related crop production value chains.

3.4. Comparison with other studies

Mogensen et al. (2014) suggested that the GWP_{100} (excluding soil C change), in kg CO_2/t DM for maize was 224, while grass-clover= 404 and ryegrass= 503, which was close to the values found in this study. Similarly, Knudsen et al. (2014) reported that the carbon footprint for winter wheat (conventional) ranged from 297 to 478 kg CO_2 eq/t DM/y, assessed for three different locations with different agro-climatic conditions. If the result for straw has to be compared on the basis of carbon footprint of winter wheat, our study gave 319 kg CO_2 eq/t DM/y for the crop. Tuomisto et al. (2012) reported this to be 401 kg CO_2 eq/ t DM for winter wheat, and in the similar range in Kramer et al. (1999). Likewise, it was in the range of 222-692 kg CO_2 eq/ t DM for wheat production in other European countries (Björnsson et al., 2013; Nemecek et al., 2011; Vellinga et al., 2013). In Vellinga et al. (2013) a constant level of soil C sequestration (i.e 30 kg C) was assumed. In contrast, Mondelaers et al. (2009) reported a lower carbon footprint for wheat production in Europe (approximately 293 kg CO_2eq/ t DM). The impact for winter wheat were even higher up to 735-879 kg CO_2eq/t DM of the grain (Korsaeth et al., 2012; Roer et al., 2012), even with the straw incorporated to field. The impact calculated for the removed straw in the same study was 270 kg CO_2eq/t DM. In the case of corn, Jayasundara et al. (2014) reported that the impact ranged from 243 to 353 kg CO_2eq/t DM, which is fairly comparable with results calculated by excluding the SOC change in our study. Most of these studies calculated the impact per ton of grain only and there were differences in the amount of agro-chemicals used in the studies.

The total NRE use for winter wheat and grass-clover was comparable with Pugesgaard et al. (2015) (13.8 and 15.7 GJ/ha/y respectively). For winter wheat production the energy demand was 3.7 GJ eq/t DM (Nemecek et al., 2011), and the differences was because of the level of intensification assumed in the crop production. For the ley production, the primary energy input was in the range of 1-1.8 GJ eq/t DM (Björnsson et al., 2013). In the same study, for winter wheat the primary energy input was 2-2.4 GJ eq/ t DM. The results varied in the range depending on the years of rotation with different yields and recirculation of nutrients (fertilizer from slurry).

The main reasons for the differences in the impact potentials (GWP, EP and NRE use) as discussed above were as follows: (i) fertilizer was a major contributor and the application rate of them were varied in the different studies, (ii) soil N_2O emissions represents the major carbon emissions associated with fertilizer application, and some study results did not include this component, (iii) the CFs for the background activities and materials were also different, and (iv) differences in the yield of biomass and SOC changes. The unit processes contribution showed that the calculated impact potentials were in accordance with other studies (Niero et al., 2015; Roer et al., 2012).

Regarding the PFWTox related to applied pesticides, Nordborg et al. (2014) reported that for maize and wheat crops it was approximately 50-150 and 260 CTUe/ha/y respectively, where the application rate were also significantly higher and the types of a.is were also different. The selection of the types of a.is showed to have significant role for varying the scores for freshwater ecotoxicity (SI, Table S3-S5). Roer et al. (2012) and Korsaeth et al. (2012) reported a higher equivalent ecotoxicity than this study. The main reason was the assumed system boundary that was able to cover the emissions related to applied pesticides and use of different active ingredients compared to this study. The type of a.is has different CFs (e.g. also demonstrated in SI Table S6).

Finally, the overall environmental impact potentials calculated per t DM showed mixed results, e.g. ryegrass and grass-clover yielded with higher impact potentials for most of the impact categories compared to the rest of the biomasses. On contrary, winter wheat straw had the highest PFWTox and maize had the highest PBD. Furthermore, with regard to the biorefinery feedstocks, the selected biomasses varied based on the total carbohydrates content. Hence, on the basis of carbohydrate content, the total dry matter of grass-clover and ryegrass (with 65-68% per t DM) and maize (81% per t DM) that is required to deliver the equivalent quantity as in straw (with 92% per t DM) (Møller et al., 2005a) ranged from 1.4 to 1.13 t DM respectively. In addition, in terms of crude protein content, grass-clover and ryegrass had highest (16.5% per t DM), whereas lowest in straw (3% per t DM) and maize (7.9% per t DM). These qualities are important in the context of producing desirable biobased products from biorefineries. The environmental burdens of the biomasses based on their chemical compositions thus also vary accordingly, with the above stated dry matter of the respective biomasses

3.5. Sensitivity analysis focusing on GWP

Sensitivity analyses are to assess the uncertainties with respect to the basic scenario.

3.5.1. Effect of indirect land use change:

In LCA studies effect of indirect land use change (iLUC) is generally defined in terms of changes in the GHG emissions (Searchinger et al., 2008). Considering the uncertainties in the iLUC models (Berndes et al., 2003), in the current study two different iLUC factors were assumed: 1.73 t CO_2eq/ha (Audsley et al., 2009) and 1.43 t CO_2eq/ha (Schmidt and Muños, 2014). The net GWP_{100} was thus approximately higher by 40-66% after the iLUC factors were included (Table 7).

3.5.2. Effect of the temporal perspective of emissions:

Very few LCA studies have made a distinction between different timings of emissions (Petersen et al., 2013; Schmidt and Brandao, 2013) when calculating carbon footprints (and LCAs). With regard to SOC changes, the added carbon to the soil, e.g. from biomass residues are released to atmosphere in different quantities over a longer period. As reported in Petersen et al. (2013) after 20 years, the C-tool simulation showed a continued soil C loss toward a new steady state and the yearly soil C losses were lower. Thus, the time perspective chosen to evaluate the C sequestration is relevant. The emission reduction potential because of SOC change was thus 9.7% in 100 years, whilst was 19.8% in 20 years (Petersen et al., 2013). With regard to such variations included in this study, it was found that the SOC was doubled in 20 years compared to the basic scenario (Table 7). This was also presented with similar findings in Knudsen et al. (2014).

3.5.3. Effect of changing the type of N-fertilizer:

Compared to the use of CAN, if potassium-nitrate was applied to the field then the net GWP_{100} was found increasing by an average factor of 1.11 for the selected biomasses (Table 7). The selection of CAN compared to potassium nitrate alone would lower the impact potential by 78%, however this would be higher by 19% compared to the use of urea (Table 5 and Table 7).

3.5.4. Straw removal using consequential approach:

The consequences of removing straw, instead of ploughing it back into the field (Petersen and Knudsen, 2010) are generally argued in two major areas: (i) displacement of nutrient (N,P,K) (Nguyen et al., 2013; Schmidt and Brandao, 2013) and (ii) loss of SOC (Dick et al., 1998). In this context, assuming that 30% of N and 100% for P and K contents of straw are available to the crops from the SOM (Nguyen et al., 2013), the removal of straw would add 25 kg CO_2 eq/t DM. Likewise, the avoidance of soil C sequestration was 139 kg CO_2eq/t DM of the straw removed (Table 7). This was in similar range as reported in Petersen and Knudsen (2010) and Parajuli et al. (2014).

Table 7: Sensitivity analysis with respect to the basic scenario

4. Conclusions

The environmental impacts in case of GWP and NRE showed the same picture and ranking for the crop biomasses (highest for ryegrass, grass-clover and maize), whereas freshwater ecotoxicity (computed based on pesticides emissions at farm level) and the potential biodiversity damages showed another picture. Straw turned out with highest PFWTox and maize had the highest negative effect to the biodiversity. The results also showed the effect of including soil carbon changes to the GWP. On an average about 35% of net GHG emissions related to ryegrass and grass-clover were mitigated because of SOC change.

The study focuses on individual crops, even though the crops in practice are cultivated in a complete rotation cycle with other crops, which might affect the performance of the crops. The N losses and soil C changes in the current study were estimated and allocated to the single crops and uncertainties were discussed. In the current study, the grasses were grown for 2 years in a crop rotation, but it might be relevant to study the effect of growing the grasses several years or as even as permanent grass, and to study the effect of increased harvest frequencies and reduced fertilizer and pesticide use or the demand in biorefinery sectors.

Finally, the study highlights that environmental sustainability assessment of biomass production based on a single set of environmental impact category (e.g. GWP) could mislead the prioritization of biomass, thus it is relevant to undertake LCAs considering a wider set of environmental impact categories.

Acknowledgements

This article is written as part of a PhD study at the Department of Agroecology, Aarhus University (AU), Denmark. The study is co-funded by the Bio-Value Platform (http://biovalue.dk/), funded under the SPIR initiative by the Innovation Fund Denmark, case no: 0603-00522B, and the Aarhus University BioBase Research Platform. The first author would like to thank the Graduate School of Science and Technology, AU for the PhD scholarship. Sincere thanks to Prof. Per Kudsk and Dr. Lise Nistrup Jørgensen (Department of Agroecology section for Crop Health, AU); and Poul Henning Petersen from the Agro Food Park, Denmark for their valuable advise, particularly on the related pesticides applications and their timings. We also would like to thank to the reviewers for their constructive suggestions provided to the study. Finally, the first author also would like to thank Jesper Overgård Lehmann (office colleague) for the related supports to this study, and the authors thank the www.dNmark.org research alliance, funded by the Innovation Fund Denmark (ref. 12-132421), for support to the modelling of nitrogen and carbon dynamics.

Reference List

Agri-footprint, 2014. Agri-footprint: Methodology and basic principles. Version 1.0. Blonk Agri-footprint BV. The Netherlands. 1-36.https://www.pre-sustainability.com/download/agri-footprint-methodology-and-basic-principles.pdf (accessed May 20, 2014).
Audsley, E., Brander, M., Chatterton, J.C., Murphy-Bokern, D., Webster, C., Williams, A.G., 2009. How low can we go? An assessment of greenhouse gas emissions from the UK food system and the scope reduction by 2050. Report for the WWF and Food Climate Research Network. 2014. 80.http://dspace.lib.cranfield.ac.uk/handle/1826/6503 (accessed Oct 28, 2014).
Benbi, D.K., Boparai, A.K., Brar, K., 2014. Decomposition of particulate organic matter is more sensitive to temperature than the mineral associated organic matter. Soil Biology and Biochemistry 70, 183-192.
Berndes, G., Hoogwijk, M., van den Broek, R., 2003. The contribution of biomass in the future global energy supply: a review of 17 studies. Biomass Bioenerg 25, 1-28.
Birkved, M., Hauschild, M.Z., 2006. PestLCI - A model for estimating field emissions of pesticides in agricultural LCA. Ecological Modelling 198, 433-451.
Björnsson, L., Prade, T., Lantz, M., Börjesson, P., Svensson, S.-E., Eriksson, H., 2013. Impact of biogas energy crops on greenhuse gas emissions, soil organic matter and food crop production-a case study on farm level. Report No 2013:27, f3. The Swedish Knowledge Centre for Renewable Transportation Fuels.http://www.f3centre.se/sites/default/files/f3_report_2013-27_biogas_energy_crops_140407.pdf (accessed Feb 29, 2016).
Brentrup, F., Kusters, J., Kuhlmann, H., Lammel, J., 2004. Environmental impact assessment of agricultural production systems using the life cycle assessment methodology - I. Theoretical concept of a LCA method tailored to crop production. European Journal of Agronomy 20, 247-264.
Dalgaard, T., Halberg, N., Porter, J.R., 2001. A model for fossil energy use in Danish agriculture used to compare organic and conventional farming. Agr Ecosyst Environ 87, 51-65.
De Schryver, A.M., Goedkoop, M.J., Leuven, R.S.E.W., Huijbregts, M.A.J., 2010. Uncertainties in the application of the species area relationship for characterisation factors of land occupation in life cycle assessment. Int J LCA 15, 682-691.
Dick, W.A., Blevins, R.L., Frye, W.W., Peters, S.E., Christenson, D.R., Pierce, F.J., Vitosh, M.L., 1998. Impacts of agricultural management practices on C sequestration in forest-derived soils of the eastern Corn Belt. Soil Till Res 47, 235-244.
Dijkman, T.J., Birkved, M., Hauschild, M.Z., 2012. PestLCI 2.0: a second generation model for estimating emissions of pesticides from arable land in LCA. International Journal of Life Cycle Assessment 17, 973-986.
EEA, 2013. EMEP/EEA air pollutant emission inventory guidebook 2013. Copenhagen, Denmark. 1-43.http://www.eea.europa.eu/publications/emep-eea-guidebook-2013 (accessed April 12, 2014).
Ellermann, T., Andersen, H.V., Bossi, R., Brandt, J., Christensen, J.H., Frohn, L.M., Geels, C., Kemp, K., Løfstrøm, P., Mogensen, B.B., Monies, C., 2005. Atmosfærisk deposition 2005: NOVANA. DMU Report no.595. 1-69.http://www2.dmu.dk/Pub/FR595.pdf (accessed Mar 12, 2014).
Elsgaard, L., Olesen, J.E., Hermansen, J.E., 2010. Greenhouse gas emissions from cultivation of winter wheat and winter rapeseed for biofuels and from production of biogas from manure. Denmark. 30.http://pure.au.dk/portal/files/43999218/726859.pdf (accessed Oct 3, 2015).
Environdec, 2015. EPD Method. 2015.http://www.environdec.com/sv/ (accessed Feb 02, 2015).
Eriksen, J., Vinther, F.P., Soegaard, K., 2004. Nitrate leaching and N 2-fixation in grasslands of different composition, age and management. Journal of Agricultural Science 142, 141-151.

European Commission, 2012a. Characterisation factors of the ILCD recommended life cycle impact assessment methods. Database and supporting information. >RC. Luxembourg. . 10 Luxembourg. 85727.http://eplca.jrc.ec.europa.eu/uploads/LCIA-characterization-factors-of-the-ILCD.pdf (accessed Jan 5, 2016).
European Commission, 2012b. Eurostat: Agricultural census in Denmark. European Commission, Brussels, Belgium.http://ec.europa.eu/eurostat/statistics-explained/index.php/Agricultural_census_in_Denmark (accessed Mar 06, 2015).
European Commission, 2015. Product Environmental Footprint (PEF). News. European Commission, Brussels, Belgium.http://ec.europa.eu/environment/eussd/smgp/ef_news.htm (accessed Feb 4, 2016).
Fantke, P.E., Huijbregts, M., Margni, M., Hauschild, M., Jolliet, O., McKone, T., Rosenbaum, R., Meent, D.v.d., 2015. USEtox® 2.0 User Manual (Version 2). UNEP/SETAC scientific consensus model for characterizing human toxicological and ecotoxicological impacts of chemical emissions in life cycle assessment. USEtox® Team.http://usetox.org (accessed Nov 15, 2015).
Fødevareministeriet., 2008. Jorden - en knap ressource: Fødevareministeriets rapport om samspillet mellem fødevarer, foder og bioenergi. Copenhagen, Denmark. 184.http://mfvm.dk/footermenu/publikations-database/publikation/pub/hent-fil/publication/jordeb-en-knap-ressource/ (accessed Oct 15, 2015).
FORCE Technology, 2010. Biolex Database.Park Alle 345, DK-2605 Brøndby, Denmark.http://www.biolexbase.dk/ (accessed Dec 15, 2015).
Guo, L.B., Gifford, R.M., 2002. Soil carbon stocks and land use change: a meta analysis. Global Change Biology 8, 345-360.
Hamelin, L., 2011. Inventory report for modelling direct land use changes of perennial and annual crop in Denmark. Version 0. Presented for the CEESA WP5 report. University of Southern Denmark, Denmark.http://www.ceesa.plan.aau.dk/digitalAssets/114/114492_24178_lci-report---direct-luc-data-for-selected-e-crops-v18-09-11-2010-ceesa.pdf (accessed Nov 17, 2014).
Hamelin, L., Jørgensen, U., Petersen, B.M., Olesen, J.E., Wenzel, H., 2012. Modelling the carbon and nitrogen balances of direct land use changes from energy crops in Denmark: a consequential life cycle inventory. Global Change Biology Bioenergy 4, 889-907.
Hansen, M.N., Summer, S.G., Hutchings, N.J., Sorensen, P., 2008. Emission factors for ammonia evaporation during storage and application of manure: Emission factors for the calculation of ammonia volatilization city storage and application of animal manure. DJF Husdyrbrug 84. 38.http://pure.agrsci.dk:8080/fbspretrieve/2424282/djfhus84.pdf (accessed March 12, 2015).
Hauggaard-Nielsen, H., Lachouani, P., Knudsen, M.T., Ambus, P., Boelt, B., Gislum, R., 2016. Productivity and carbon footprint of perennial grass–forage legume intercropping strategies with high or low nitrogen fertilizer input. Science of The Total Environment 541, 1339-1347.
Hauschild, M., Goedkoop, M., Guinée, J., Heijungs, R., Huijbregts, M., Jolliet, O., Margni, M., De Schryver, A., Humbert, S., Laurent, A., Sala, S., Pant, R., 2013. Identifying best existing practice for characterization modeling in life cycle impact assessment. Int J LCA 18, 683-697.
Høgh-Jensen, H., Kristensen, E.S., 1995. Estimation of Biological N2 Fixation in a Clover-Grass System by the 15N Dilution Method and the Total-N Difference Method. Biological Agriculture & Horticulture 11, 203-219.
IPCC, 2006. 2006 IPCC Guidelines for National Greenhouse Gas Inventories, Prepared by the National Greenhouse Gas Inventories Programme, Eggleston H.S., Buendia L., Miwa K., Ngara T. and Tanabe K. (eds). Published: IGES, Japan. 4. 11.11- 11.24.http://www.ipcc-nggip.iges.or.jp/public/2006gl/index.html (accessed Sep 27, 2012).
Jayasundara, S., Wagner-Riddle, C., Dias, G., Kariyapperuma, K.A., 2014. Energy and greenhouse gas intensity of corn (Zea mays L.) production in Ontario: A regional assessment. Canadian Journal of Soil Science 94, 77-95.
Jørgensen, K., (Edts)., Hummelmose, A.B., Pedersen, B.K., Wøyen, T.T., Maegaard, E., Jørgensen, K., Bruun, L.K., 2011. Budgetkalkuler 2010-pr. oktober 2010. SEGES, Aarhus, Denmark.

Denmark.https://www.landbrugsinfo.dk/Oekonomi/Budgetkalkuler/Sider/Budgetkalkuler_2010-2011_okt10.aspx (accessed Feb 5, 2015).
Jørgensen, U., Sørensen, P., Adamsen, A.P., Kristensen, I.T., 2008. Energi fra biomasse-Ressourcer og teknologier vurderet i et regionalt perspektiv. Aarhus University, Aarhus, Denmark. 78.
Kircher, M., 2012. The transition to a bio-economy: national perspectives. Biofuels, Bioproducts and Biorefining 6, 240-245.
Kirchmann, H., Johnston, A.E.J., Bergström, L.F., 2002. Possibilities for Reducing Nitrate Leaching from Agricultural Land. AMBIO: A Journal of the Human Environment 31, 404-408.
Knudsen, M.T., Dennis, P., Hermansen, J.E., Cederberg, C., Herzog, F., Vale, J., Jeanneret , P., Sarthou, J.-P., Friedel, J., Balazs, Katalin , Fjellstad, W., Kainz, Max., Wolfram, S., 2016. Characterization factors from direct measures of plant species in European farmland for land use impacts on biodiversity in life cycle assessment. Under review Science of the Total Environment.
Knudsen, M.T., Meyer-Aurich, A., Olesen, J.E., Chirinda, N., Hermansen, J.E., 2014. Carbon footprints of crops from organic and conventional arable crop rotations – using a life cycle assessment approach. Journal of Cleaner Production 64, 609-618.
Korsaeth, A., Jacobsen, A.Z., Roer, A.G., Henriksen, T.M., Sonesson, U., Bonesmo, H., Skjelvåg, A.O., Strømman, A.H., 2012. Environmental life cycle assessment of cereal and bread production in Norway. Acta Agriculturae Scandinavica, Section A — Animal Science 62, 242-253.
Kramer, K.J., Moll, H.C., Nonhebel, S., 1999. Total greenhouse gas emissions related to the Dutch crop production system. Agriculture, Ecosystems & Environment 72, 9-16.
Kristensen, E.F., Grundtoft, S., 2003. Tørring af korn i lagertørringsanlæg: drift, tørringsstrategi og energiforbrug (in Danish). Danmarks JordbrugsForskning, Forskningscenter Foulum. Denmark. 8.http://web.agrsci.dk/djfpublikation/djfpdf/gvm282.pdf (accessed Dec 15, 2015).
Kristensen, T., 2015. Beregning af grovfoderudbytte på kvægbrug ud fra regnskabsdata. Intern notat til Normudvalget. Institut for Agroøkologi, Blichers Allé 20, 8830 Tjele. 26.http://dca.au.dk/fileadmin/DJF/DCA/Forside/DCArapport57.pdf (accessed Oct 7, 2015).
Larsson, M.H., Kyllmar, K., Jonasson, L., Johnsson, H., 2005. Estimating Reduction of Nitrogen Leaching from Arable Land and the Related Costs. AMBIO: A Journal of the Human Environment 34, 538-543.
Manevski, K., Børgesen, C., Andersen, M., Kristensen, I., 2015. Reduced nitrogen leaching by intercropping maize with red fescue on sandy soils in North Europe: a combined field and modeling study. Plant and Soil 388, 67-85.
Martinez-Alier, J., Munda, G., O'Neill, J., 1998. Weak comparability of values as a foundation for ecological economics. Ecological Economics 26, 277-286.
McLenaghen, R.D., Cameron, K.C., Lampkin, N.H., Daly, M.L., Deo, B., 1996. Nitrate leaching from ploughed pasture and the effectiveness of winter catch crops in reducing leaching losses. New Zealand Journal of Agricultural Research 39, 413-420.
Mikkelsen, M.H., Albrektsen, R., Gyldenkærne, S., 2011. Danish emission inventory for agriculture inventories 1985-2009. Denmark. 136.http://www2.dmu.dk/pub/fr810.pdf (accessed April 22, 2015).
Mogensen, L., Kristensen, T., Nguyen, T.L.T., Knudsen, M.T., Hermansen, J.E., 2014. Method for calculating carbon footprint of cattle feeds – including contribution from soil carbon changes and use of cattle manure. Journal of Cleaner Production 73, 40-51.
Møller, J., Thøgersen, R., Helleshøj, M.E., Weisbjer, M., Søegaard, K., Hvelplund, T., 2005a. Fodermiddltabel 2005. Sammensætning og foderværdi af fodermidler til kvæg. SEGES, Aarhus, Denmark.https://www.landbrugsinfo.dk/kvaeg/foder/sider/fodermiddeltabel_2005.aspx (accessed July 22, 2015).
Møller, J., Thøgersen, R., Kjeldsen, A., Weisbjer, M., Søegaard, K., Hvelplund, T., Børsting, C., 2000. Fodermiddltabel. Sammensætning og foderværdi af fodermidler til kvæg. SEGES, Aarhus, Denmark.https://www.landbrugsinfo.dk (accessed July 22, 2015).

Møller, J., Thøgersen, R., Kjeldsen, A., Weisbjer, M., Søegaard, K., Hvelplund, T., Børsting, C., 2005b. Fodermiddltabel 2005. Sammensætning og foderværdi af fodermidler til kvæg.https://www.landbrugsinfo.dk/kvaeg/foder/sider/fodermiddeltabel_2005.aspx (accessed July 22, 2015).
Møller, S., Christensen, T.B., Sloth, N., 2012. Næringsindhold i korn fra høsten. Videncenter for Svineproduktion. Notat nr. 1226, Denmark. Denmark. 1-16.http://vsp.lf.dk/~/media/Files/PDF%20-%20Publikationer/Notater%202012/Notat%20nr%201226.pdf (accessed Oct 7, 2015).
Møller, S., Sloth, N., 2013. Næringsindhold i korn fra høsten. Videncenter for Svineproduktion, Denmark. Denmark. 16.http://vsp.lf.dk/~/media/Files/PDF%20-%20Publikationer/Notater%202013/Notat_1334.ashx (accessed July 22, 2015).
Møller, S., Sloth, N., 2014. Næringsindhold i korn fra høsten. Videncenter for Svineproduktion, Denmark. Denmark. 18.http://vsp.lf.dk/~/media/Files/PDF%20-%20Publikationer/Notater%202014/Notat_1432.pdf (accessed Oct 7, 2015).
Mondelaers, K., Aertsens, J., Huylenbroeck, G.V., 2009. A meta-analysis of the differences in environmental impacts between organic and conventional farming. British Food Journal 111, 1098-1119.
NaturErhvervstyrelsen, 2015. Vejledning om gødsknings-og harmoniregler: Planperioden 1. august 2014 til 31. juli 2015. Agriculture and Fisheries (in Danish) Copenhagen, Denmark. 173.http://www.nordfynskommune.dk/~/media/Files/Dokumenter/Teknik%20og%20Miljoe/Natur%20og%20Miljoe/Landbrug/Vejledning%20om%20g%C3%B8dnings-%20og%20harmoniregler.pdf (accessed May 15, 2015).
Nebe, S., 2011. Bio-based economy in Europe: State of play and future potential–Part 2 Summary of position papers received in response to the European Commission\'s Public on-line Consultation. 30.https://ec.europa.eu/research/consultations/bioeconomy/bio-based-economy-for-europe-part2.pdf (accessed Nov 20, 2015).
Nemecek, T., Huguenin-Elie, O., Dubois, D., Gaillard, G., Schaller, B., Chervet, A., 2011. Life cycle assessment of Swiss farming systems: II. Extensive and intensive production. Agricultural Systems 104, 233-245.
Nemecek, T., Kägi, T., 2007. Life cycle inventories of agricultural production systems. Swiss Centre for Life Cycle Inventories,, Duebendorf, Switzerland.
Nguyen, T.L.T., Hermansen, J.E., Mogensen, L., 2013. Environmental performance of crop residues as an energy source for electricity production: The case of wheat straw in Denmark. Applied Energy 104, 633-641.
Nielsen, P., 2004. Heat and power production from straw (Produktion af kraftvarme fra halm). The Institute for Product Development, Denmark. http://www.lcafood.dk/processes/energyconversion/heatandpowerfromstraw.htm (accessed Oct 18, 2012).
Nielsen, P.H., Wenzel, H., 2007. Environmental assessment of Ronozyme® P5000 CT phytase as an alternative to inorganic phosphate supplementation to pig feed used in intensive pig production. Int J LCA 12, 514-520.
Niero, M., Ingvordsen, C.H., Peltonen-Sainio, P., Jalli, M., Lyngkjær, M.F., Hauschild, M.Z., Jørgensen, R.B., 2015. Eco-efficient production of spring barley in a changed climate: A Life Cycle Assessment including primary data from future climate scenarios. Agricultural Systems 136, 46-60.
Nordborg, M., Cederberg, C., Berndes, G., 2014. Modeling Potential Freshwater Ecotoxicity Impacts Due to Pesticide Use in Biofuel Feedstock Production: The Cases of Maize, Rapeseed, Salix, Soybean, Sugar Cane, and Wheat. Environmental Science & Technology 48, 11379-11388.
Oksen, A., 2012. Landbrugets driftsresultater 2011, Tabel 4. Malkekvægsbrug - inddelt efter besætningsstørrelse. Landbrugets driftsresultater 2011, Denmark. 1-10.https://www.landbrugsinfo.dk/Oekonomi/Oekonomiske-analyser/Driftsresultater-priser-prognoser/Sider/Landbrugets-driftsresultater-2011.aspx (accessed Sep 22, 2015).
Ørum, J.E., Samsøe-Petersen, L., 2014. Bekæmpelsesmiddelstatistik 2013: behandlingshyppighed og belastning. Miljøstyrelsen, Copenhagen, Denmark.

66.http://www2.mst.dk/Udgiv/publikationer/2014/12/978-87-93283-33-6.pdf (accessed Dec 15, 2015).
Parajuli, R., Dalgaard, T., Jørgensen, U., Adamsen, A.P.S., Knudsen, M.T., Birkved, M., Gylling, M., Schjørring, J.K., 2015. Biorefining in the prevailing energy and materials crisis: a review of sustainable pathways for biorefinery value chains and sustainability assessment methodologies. Renew Sust Energ Rev 43, 244-263.
Parajuli, R., Løkke, S., Østergaard, P.A., Knudsen, M.T., Schmidt, J.H., Dalgaard, T., 2014. Life Cycle Assessment of district heat production in a straw fired CHP plant. Biomass and Bioenergy 68, 115-134.
Petersen, B.M., Knudsen, M.T., 2010. Consequences of straw removal for soil carbon sequestration of agricultural fields, Using soil carbon in a time frame perspective. Faculty of Agricultural Sciences, Aarhus University, Aarhus, Denmark. 1-49.http://pure.au.dk/portal/en/publications/consequences-of-straw-removal-for-soil-carbon-sequestration-of-agricultural-fields(ab049e95-9471-463d-97b7-69635ec81518).html (accessed Nov 15,, 2015).
Petersen, B.M., Knudsen, M.T., Hermansen, J.E., Halberg, N., 2013. An approach to include soil carbon changes in life cycle assessments. Journal of Cleaner Production 52, 217-224.
Philben, M., Ziegler, S.E., Edwards, K.A., Kahler, R., Benner, R., 2016. Soil organic nitrogen cycling increases with temperature and precipitation along a boreal forest latitudinal transect. Biogeochemistry 127, 397-410.
Powlson, D.S., Whitmore, A.P., Goulding, K.W.T., 2011. Soil carbon sequestration to mitigate climate change: a critical re-examination to identify the true and the false. European Journal of Soil Science 62, 42-55.
PRé Consultants, 2015. SimaPro 8.0.4. Pre Consultants. Amersfort. The Netherlands. 2013.http://www.pre-sustainability.com/simapro-lca-software (acccessed Nov 25, 2015).
Pugesgaard, S., Schelde, K., Larsen, S.U., Laerke, P.E., Jørgensen, U., 2015. Comparing annual and perennial crops for bioenergy production - influence on nitrate leaching and energy balance. GCB Bioenergy 7, 1136-1149.
Ragauskas, A.J., Williams, C.K., Davison, B.H., Britovsek, G., Cairney, J., Eckert, C.A., Frederick, W.J., Jr., Hallett, J.P., Leak, D.J., Liotta, C.L., Mielenz, J.R., Murphy, R., Templer, R., Tschaplinski, T., 2006. The path forward for biofuels and biomaterials. Science 311, 484-489.
Rebitzer, G., Ekvall, T., Frischknecht, R., Hunkeler, D., Norris, G., Rydberg, T., Schmidt, W.P., Suh, S., Weidema, B.P., Pennington, D.W., 2004. Life cycle assessment part 1: framework, goal and scope definition, inventory analysis, and applications. Environ Int 30, 701-720.
Roer, A.-G., Korsaeth, A., Henriksen, T.M., Michelsen, O., Strømman, A.H., 2012. The influence of system boundaries on life cycle assessment of grain production in central southeast Norway. Agricultural Systems 111, 75-84.
Rosenbaum, R., Bachmann, T., Gold, L., Huijbregts, M.J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H., MacLeod, M., Margni, M., McKone, T., Payet, J., Schuhmacher, M., van de Meent, D., Hauschild, M., 2008. USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. Int J LCA 13, 532-546.
Schmidt, J.H., Brandao, M., 2013. LCA screening of biofuels-iLUC, biomass manipulation and soil carbon. Copenhagen, Denmark. . 3-97.http://concito.dk/files/dokumenter/artikler/biomasse_bilag1_lcascreening.pdf (accessed May 12, 2013).
Schmidt, J.H., Dalgaard, R., 2012. National and farm level carbon footprint of milk-Methodology and results for Danish and Swedish milk 2005 at farm gate. Arla Foods, Aarhus, Denmark. 1-119.http://lca-net.com/files/Arla-Methodology_report_20120724.pdf (accessed May 15, 2014).
Schmidt, J.H., Muños, I., 2014. The carbon footprint of Danish production and consumption: Literature review and model calculations. Energistyrelsen. Copenhagen, Denmark. 1-119.http://vbn.aau.dk/files/196725552/_dk_carbon_footprint_20140305final.pdf (accessed Feb 02, 2016).

Schmidt, M.W.I., Torn, M.S., Abiven, S., Dittmar, T., Guggenberger, G., Janssens, I.A., Kleber, M., Kogel-Knabner, I., Lehmann, J., Manning, D.A.C., Nannipieri, P., Rasse, D.P., Weiner, S., Trumbore, S.E., 2011. Persistence of soil organic matter as an ecosystem property. Nature 478, 49-56.
Searchinger, T., Heimlich, R., Houghton, R.A., Dong, F., Elobeid, A., Fabiosa, J., Tokgoz, S., Hayes, D., Yu, T.H., 2008. Use of U.S. croplands for biofuels increases greenhouse gases through emissions from land-use change. Science 319, 1238-1240.
SEGES, 2015a. Farmtal Online. Vinterhvede (1.års). SEGES, Agro Food Park, Aarhus, Denmark.https://farmtalonline.dlbr.dk/Kalkuler/VisKalkule.aspx?Prodgren=K_1150&Forudsaetninger=31-12-2015;K_1150;1;1;2;1;2;1;1;1;3;1;n;n;0;n (accessed Feb 04, 2016).
SEGES, 2015b. Middeldatabasen. SEGES, Agro Food Park, Aarhus, Denmark.https://www.middeldatabasen.dk/ (accessed Nov 09, 2015).
Simmelsgaard, S.E., 1998. The effect of crop, N-level, soil type and drainage on nitrate leaching from Danish soil. Soil Use and Management 14, 30-36.
Sommer, S.G., Schjoerring, J.K., Denmead, O.T., 2004. Ammonia Emission from Mineral Fertilizers and Fertilized Crops, Advances in Agronomy. Academic Press, pp. 557-622.
Statistics Denmark, 2013. HST77: Harvest by region, crop and unit. tatistik om landbrug, gartneri og skovbrug,Denmark.http://www.statistikbanken.dk/statbank5a/SelectVarVal/Define.asp?Maintable=HST77&PLanguage=1 (accessed Jul 07, 2015).
Taghizadeh-Toosi, A., Christensen, B.T., Hutchings, N.J., Vejlin, J., Kätterer, T., Glendining, M., Olesen, J.E., 2014. C-TOOL – A soil carbon model and its parameterisation. Ecological Modelling 292, 11-25.
Thøgersen, R., Kjeldsen, A.M., 2014. Grovfoder 2014.https://www.landbrugsinfo.dk/Kvaeg/Tal-om-kvaeg/Sider/fod2014.aspx (accessed Mar 23, 2015).
Thøgersen, R., Kjeldsen, A.M., 2015. Grovfoder 2015. https://www.landbrugsinfo.dk/Kvaeg/Tal-om-kvaeg/Sider/fod2015.aspx (accessed Mar 22, 2015)
Thomsen, I.K., Hansen, J.F., Kjellerup, V., Christensen, B.T., 1993. Effects of cropping system and rates of nitrogen in animal slurry and mineral fertilizer on nitrate leaching from a sandy loam. Soil Use and Management 9, 53-57.
Thorup-Kristensen, K., Magid, J., Jensen, L.S., 2003. Catch crops and green manures as biological tools in nitrogen management in temperate zones, Advances in Agronomy. Academic Press, pp. 227-302.
Tidåker, P., Sundberg, C., Öborn, I., Kätterer, T., Bergkvist, G., 2014. Rotational grass/clover for biogas integrated with grain production – A life cycle perspective. Agricultural Systems 129, 133-141.
Tuomisto, H.L., Hodge, I.D., Riordan, P., Macdonald, D.W., 2012. Comparing global warming potential, energy use and land use of organic, conventional and integrated winter wheat production. Annals of Applied Biology 161, 116-126.
Vellinga, T.V., Blonk, H., Marinussen, M., Van Zeist, W., De Boer, I., 2013. Methodology used in feedprint: a tool quantifying greenhouse gas emissions of feed production and utilization. Wageningen UR Livestock Research.http://edepot.wur.nl/254098 (accessed Jun 12, 2015).
Vils, E., Sloth, N., 2003. Videncenter for Svineproduktion, . Næringsindhold i korn fra høsten Denmark. 12.http://vsp.lf.dk/Publikationer/Kilder/Notater/2004/0345.aspx?full=1 (accessed Oct 7, 2015).
Vinther, F., 2005. SimDen–A simple empirical model for quantification of N2O emission and denitrification. Tjele, Denmark. 4.http://orgprints.org/5759/ (accessed Apr 22, 2015).
Watson, C.A., Bengtsson, H., Ebbesvik, M., Løes, A.K., Myrbeck, A., Salomon, E., Schroder, J., Stockdale, E.A., 2002. A review of farm-scale nutrient budgets for organic farms as a tool for management of soil fertility. Soil Use and Management 18, 264-273.
Weidema, B.P., Bauer, C., Hischier, R., Mutel, C., Nemecek, T., Reinhard, J., Vadenbo, C., Wernet, G., 2013. Overview and methodology. Data quality guideline for the ecoinvent database version 3. Ecoinvent Report 1(v3). St. Gallen: The ecoinvent Centre. Swiss Centre for Life Cycle Inventories.

159.http://vbn.aau.dk/ws/files/176769045/Overview_and_methodology.pdf (accessed Feb 12, 2015).

List of Tables:

Table 1: Input-output for the crop production, per ha per year

Particulars	Unit	Amount				Comments/Remarks
		Maize	Grass-clover	Ryegrass	Winter wheat	
Inputs						
Seed[a]	kg seed ha^{-1}	13	8	9	179	See footnotes
Synthetic fertilizer	kg ha^{-1}					(NaturErhvervstyrelsen, 2015)
N		141	193[b]	279[b]	144	
P		45	33	32	19	
K		137	327	407	71	
Lime	kg ha^{-1}	167	84	84	167	(Hamelin et al., 2012)
Pesticides	kg a.is ha^{-1}	0.21	0.03	0.03	1.72	
Lubricant oil,	l ha^{-1}	18	11	11	14	(Dalgaard et al., 2001)
Direct primary energy input (diesel)[d]	MJ ha^{-1}	4955	3644	3794	3126	Field operations = a+b+d. See footnotes and section 2.4.1
a. Field preparation[c]	MJ ha^{-1}	3064	992	992	2135	Tillage + agro-chemicals applications
b. Harvesting + loading and handling[d]	MJ ha^{-1}	1891	2652	2802	991	
c. Transport	t km ha^{-1}					CF from Weidema et al. (2013)
- seeds[e]	t km ha^{-1}	2.5	1.6	1.8	35.8	
- agro-chemicals[f]	t km ha^{-1}	95	149	186	89	
- biomass (field to farm)[g]	t km ha^{-1}	30	23	26	27	

d. Drying						(Kristensen and Grundtoft, 2003)
- Electricity	kWh ha^{-1}	-	-	-	111	
- Heat	MJ ha^{-1}	-	-	-	364	
Output						
Net biomass yield	t DM ha^{-1}	9.91	7.71	8.75	9.1	
Net biomass yield[h]	GJ ha^{-1}	161	108	121	48*	

[a] Seed quantity after Hamelin et al. (2012). (DM content based on Thøgersen and Kjeldsen (2014)).

- Maize (kg seed/ha) = 4.4*10^{-4} kg per kg (wet) primary yield (PY) * kg PY/0.347 kg DM * t DM yield * 10^{3} kg DM/ha.
- Grass-clover: (kg seed/ha) = 3.7*10^{-4} kg per kg (wet) PY * kg PY/0.35 kg DM * t DM yield * 10^{3} kg DM/ha. Proportion of grass: clover (80:20) assumed for the seed mass.
- Ryegrass: similar to grass-clover (100 % of the grass-seed).
- Winter wheat: 2.6*10^{-4} kg per kg (wet) PY* kg PY/0.85 kg DM * t DM yield.

[b] N-fertilizer: Grass-clover and ryegrass = N-norm – reduced quota (40.5 kg N/ha/y) in the crop following the grasses (NaturErhvervstyrelsen, 2015).

[c] Includes tillage and application of agro-chemicals. Heating value of diesel= 35.95 MJl^{-1}, Density= 0.84 kg/l (Weidema et al., 2013).

[d] Calculation for the loading and handling :

[†] Baling (straw, grass-clover and ryegrass)= DM/ha * bale/160 kgfw/%DM kg DM *1000 kg/t * 0.23 = bales/ha Diesel = 0.743 kg/bale (Hamelin et al., 2012).

[ρ] Bale loading= (Number of bales/ha /0.23) * 0.0811 kg/bale (Hamelin et al., 2012). Diesel = 3 l/ha (Dalgaard et al., 2001).

[↓] Loading for maize = 0.119 l m^{-3} fodder (Møller et al., 2000). Fodder (m^{3}) = DM/ha * kgfw/DM% * 0.004 m^{3} fodder loading/kgfw *1000 kg/t (Hamelin et al., 2012). Loading for winter wheat is for the grain only.

[e] Mass of seed * distance (= 200 km) (Parajuli et al., 2014).

[f] Fertilizer + lime + pesticides) * distance (200 km)

[g] t DM * 3 km. Distance assumed, as in Mogensen et al. (2014).

[h] Lower heating value (MJ/kg): maize= 19 (FORCE Technology, 2010), grass-clover=11.8 (Jørgensen et al., 2008), ryegrass=16 (Fødevareministeriet., 2008) and straw = 15.01(Nielsen, 2004). *Values represent for straw.

Table 2: Carbon sequestration as a result of soil C changes between the reference land use and the production of the selected crops

Parameters/Crop types	Unit	Maize	Grass-clover	Ryegrass	Winter wheat	Barley[a]
Biomass yield	t DM/ha/y	9.91	7.71	8.75	5.87 (grain)	4.08
Straw (100% removed, excluding barley)[a]	t DM/ha/y	-	-	-	3.23 (straw)	2.24
Total available non-harvestable residues						
Root[b]	t DM/ha/y	2.06	9.02	10.23	4.33	1.77
Stubble, chaff, straw left in the field[c]	t DM/ha/y	1.75	3.31	3.75	3.91	4.58
Total plant residues[d]	t DM/ha/y	3.81	12.32	13.98	8.25	6.36
Plant residues N to soil[e]	kg N/ha/y	34	264	299	75	45
C input from crop residue[f]	kg C/ha/y	1751	5668	6429	3794	2924
C input to soil compared to reference crop[g]	kg C/ha	-1173	2744	3505	870	-
Emissions from soil C change (100-years)[h]	kg CO_2/ha/y	417	-976	-1247	-310	-

Assumptions:

[a] Barley represent the reference land use and 100% of the straw from the crops are incorporated into the soil.

[b] Harvest index (alpha) and root mass (beta) of the selected crops are based on Taghizadeh-Toosi et al. (2014).

[c] Calculated as: Total plant residues - Root residues.

[d] Total Plant residues = Crop yield * Parameter† for stubble+root/(net yield). Parameter†: maize (0.384), grass-clover and ryegrass (1.597), winter wheat (1.406) (Mikkelsen et al., 2011).

[e] Calculated from the “Total plant residue”, see footnote [d]). Norms of crude protein (% DM) in (stubble/straw, root), respectively = maize (7.8, 3.8); grass-clover and ryegrass (14.7, 12.9); winter wheat (3.3, 7.8) and barley (4 and 7.8) (Mikkelsen et al., 2011).

[f] Calculated from the total C assimilation (Taghizadeh-Toosi et al., 2014).

[g] C input from the selected crops minus C input from the reference crop.

[h] 9.7% of the SOC change (Petersen et al., 2013) * mol.weight of CO_2 to C (44/12). Negative value here indicates the soil C sequestration.

Table 3: Emission factors used in the study

Parameters	Pollutants	Unit related	Emission factors/values	Reference
kg NH_3-N	N-fertilizer volatilization	kg N/ha/y	0.02	(EEA, 2013; Nemecek and Kägi, 2007);
kg NH_3-N	Plant (crops)	kg N/ha residues[a]	2 (cereals) 0.5 (grasses)[b]	(Sommer et al., 2004).
NO_x-N: NH_3-N[c]			12:88	(Schmidt and Dalgaard, 2012)
N_2O-N_{direct}	Synthetic N Crop residues[d]	kg N/ha kg N/ha	0.01 0.01	(IPCC, 2006)
N_2O-$N_{indirect}$	From leaching From NH_3	kg NO_3-N kg NH_3-N	0.0075 0.01	(IPCC, 2006)
P-uptake by plant[e]	Maize Winter wheat Grass-clover and Ryegrass	g P/kg DM g P/kg DM g P/kg DM	2.6 2.8[†] and 0.9[††] 4	(Hamelin, 2011; Møller et al., 2000)
P losses[f]	All crops	Surplus[f], g P/ha	0.05	(Nielsen and Wenzel, 2007)

[a] See kg N/ha from residues (Table 2).

[b] NH_3 emission for grasses: average of summer and spring application for grasses) (Hansen et al., 2008).

[c] NO_x-N = (NO+NO_2), where NO_2 is assumed to be negligible, and calculated as NO_x-N: NH_3-N.

[d] fraction of total area under crop that are renewed every 2 years ($Frac_{renew}$) = 0.5 (IPCC, 2006) is multiplied to the N_2O-N_{direct} emission from the crop residues.

[e] P-uptake by plant in winter wheat are respectively for the [†] primary and [††]secondary yields.

[f] P surplus = P-input from fertilizer minus P uptake by plant.

Table 4: N balances and emissions, per 1 ha of the crop production

Particulars	Unit	Amount				Comments/Remarks
		Maize	Grass-clover	Ryegrass	Winter wheat	
Total N-input[a]	kg N $ha^{-1}y^{-1}$	156	288	294	162	See footnotes
Output[b]	kg N $ha^{-1}y^{-1}$	125	204	231	119	See footnotes
Field balance	kg N $ha^{-1}y^{-1}$	31	84	63	42	N_{input}-N_{output}
N losses	kg N $ha^{-1}y^{-1}$					
NH_3-N		4.8	4.4	6.1	4.9	Table 3
NOx-N		0.7	0.6	0.8	0.7	Table 3
Denitrification		6.2	9.8	13.3	8.1	(Vinther, 2005).
Soil change, N	kg N $ha^{-1}y^{-1}$	-17	25	33	5	see section 2.4.3
Potential leaching	kg N $ha^{-1}y^{-1}$	36	44	9	24	Field balance – N losses
Total N_2O-N losses (direct +indirect)	kg N $ha^{-1}y^{-1}$	2.1	3.6	4.4	2.4	Table 3
P losses	kg P $ha^{-1}y^{-11}$	2.2	1.6	1.6	0.9	Table 3

Assumptions:

[a] Total N-input = F_{SN} + $N_{fixation}$[ρ] + $N_{deposition}$[†] + N_{seed}[±].

[ρ] $N_{fixation}$ for grass-clover = 80 kg N/ha/y (Høgh-Jensen and Kristensen, 1995).

[†]N deposition = 15 kg Nha^{-1} (Ellermann et al., 2005).

[±]N_{seed} (kg N/ha/y) = 0.16 (maize); 0.17 (grass-clover); 0.19 (ryegrass); 2.8 (winter wheat), based on the crude protein content of the respective seeds (9.6, 15, 15 and 11.5% per t DM of seeds respectively) (Møller et al., 2005a) .

[b] Calculated based on Crude N and the DM yield. Crude N content (% DM)= maize =7.9; grass-clover and ryegrass = 16.5 (average of 2000-2013, based on (Møller et al., 2005a); Thøgersen and Kjeldsen (2015); Winter wheat= 10.9 and straw= 3.3. average of years 2007-2013, based on reports (Møller et al., 2012; Møller and Sloth, 2013, 2014; Vils and Sloth, 2003)).

Table 5: Environmental impact potentials for the production of the selected biomasses, per 1 ha

Environmental impacts	Units	Maize	Grass-clover	Ryegrass	Winter wheat-straw[±]
Net GWP_{100} (including soil C change)	kg CO_2 eq/ha	3119	2728	3588	492
Gross GWP_{100} (excluding soil C change)	kg CO_2 eq/ha	2701	3704	4835	551
- GWP_{100} related to N_2O-N emission	kg CO_2 eq/ha	983	1686	2060	249
- GWP related to diesel consumption[a]	kg CO_2 eq/ha	397	292	304	48
- GWP related to fertilizer production (N,P,k)[b]	kg CO_2 eq/ha	1177	1614	2236	202
- GWP related to producing N-fertilizer only	kg CO_2 eq/ha	933	1274	1843	181
EP	kg PO_4 eq/ha	14	16	15	2.24
NRE use	GJ eq/ha	18	19	25	3.2
- related to diesel consumption[a]	GJ eq/ha	5.6	4.1	4.3	0.67
PBD	PDF	0.68	0.09	0.12	0.13
PFWTox	CTU_e/ha				
- Total		771	609	651	237
- Related to applied pesticides		6	0.16	0.16	31

[±] Values for straw allocated (19%) from the total impact calculated for total cereal production.

[a] Diesel consumption related to field operations (see Table 1). CF/MJ diesel burnt in machineries = GWP_{100} (0.08 kg CO_2 eq); NRE (1.13 MJe) (Agri-footprint, 2014).

[b] CFs for the fertilizers, expressed in the order GWP (in kg CO_2eq); EP (in kg PO4 eq); and NRE use (in MJ eq) are:

- 1 kg CAN-N (NPK 26.5 at plant/RER/Economic) = 6.6; 0.021;44 (Agri-footprint, 2014).
- 1 kg P (Triple super phosphate/RER/Alloc, Def/U) = 3.3; 0.025;50 (Weidema et al., 2013).
- 1 kg K_2O-K (Potassium chloride/RER/Alloc, Def/U) = 0.7; 0.002; 8 (Weidema et al., 2013).

Table 6: Environmental impact potentials of the selected biomass feedstocks per t DM and per MJ

Environmental impacts	Unit	Maize	Grass-clover	Ryegrass	Winter wheat-straw
Net GWP_{100} (including soil C change	kg CO_2 eq/t DM	315	354	410	152
	kg CO_2 eq/MJ	0.019	0.025	0.029	0.01
Gross GWP_{100}, (excluding soil C change)	kg CO_2 eq/t DM	273	480	553	171
	kg CO_2 eq/MJ	0.017	0.034	0.039	0.011
- SOC change	kg CO_2 eq/t DM	42	-127	-142	-18
	kg CO_2 eq/MJ	$2.6*10^{-3}$	$-9.1*10^{-3}$	$-1*10^{-2}$	$-1.1*10^{-3}$
EP	kg PO_4 eq/t DM	1.44	2.04	1.76	0.61
	kg PO_4 eq/MJ	$8.9*10^{-5}$	$1.5*10^{-4}$	$1.3*10^{-4}$	$4.1*10^{-5}$
NRE Use	MJeq/t DM	1774	2400	2846	849
	MJeq/MJ	0.11	0.17	0.21	0.06
PBD	PDF/t DM	0.07	0.012	0.014	0.04
	PDF/MJ	$4*10^{-6}$	$8*10^{-7}$	$10*10^{-7}$	$3*10^{-6}$
PFWTox (related to applied pesticides)	CTU_e/t DM	0.6	0.02	0.02	9.67
	CTU_e/MJ	$3.7*10^{-5}$	$1.5*10^{-6}$	$1.3*10^{-6}$	$6.4*10^{-4}$

Table 7: Sensitivity analysis with respect to the basic scenario

Scenarios	Maize	Grass-clover	Ryegrass	Winter wheat-straw
Basic scenario:				
i. Net GWP_{100} (including soil C change), kg CO_2 eq /t DM	305	354	410	152
ii. Net GWP_{100} (kg CO_2 eq /t DM)				
a. with iLUC effect				
- iLUC factor (Audsley et al., 2009)	480	578	608	254
- iLUC factor (Schmidt and Muños, 2014)	449	539	574	236
b. with changed N fertilizer (as Potassium Nitrate)[a]	332 (121)†	400 (211)†	459 (270)†	168 (72)†
c. with changed N fertilizer (as Urea)[b]	229	220	239	107
d. using soil C sequestration in 20-years	437	-38	-41	94
iii. Impact of removing 1 t DM of straw straw removed) (kg CO_2 eq/tDM	-	-	-	161
a. Avoided soil C sequestration[c]	-	-	-	139
b. Fertilizer compensation[d, e]	-	-	-	22
- *N*				*10*
- *P*				*2*
- *K*				*9*

[a] "N fertilizer, as N, GLO, potassium nitrate, Alloc Def, U", CF adapted from Weidema et al. (2013). CF = 8.47 kg CO_2 eq/kg N. †Values shown in the parenthesis represents the specific impact of producing the N-fertilizer only.

[b] "Urea, as % CO(NH2)2 (NPK 46.6-0-0) (RER/Economic). CF = 1.24 kg CO_2-eq/ kg N (Agri-footprint, 2014).

[c] Soil C sequestration= C content in straw (Taghizadeh-Toosi et al., 2014) * 0.85 * emission reduction potential (Petersen et al., 2013)= 0.46*1 t*0.85*9.7%= 38.99 kg C = 139 kg CO_2-eq.

[d] Compensation based on nutrient content in the removed straw (Møller et al., 2005b):

- N = 30% * kg N in straw (Nguyen et al., 2013) = 30%* 0.6% * 1 t * 0.85.
- P = kg P in straw * Ratio of mol. wt = 0.09% * 1 t straw * 0.8.
- K = kg of K in 1 t of straw (85% DM) * (Ratio of mol. wt) = 1.5% * 1 (kg) * 0.85.

[e] Types of fertilizer and CFs are shown in Table 5.

Figure captions:

Figure 1: The farm gate system boundary defined for the biomass production**.**

Figure 2: Environmental impact potentials of producing the selected biomass types (GWP_{100} includes soil C change).

Figure 3: Environmental impact potentials in the related biomass production value chains.

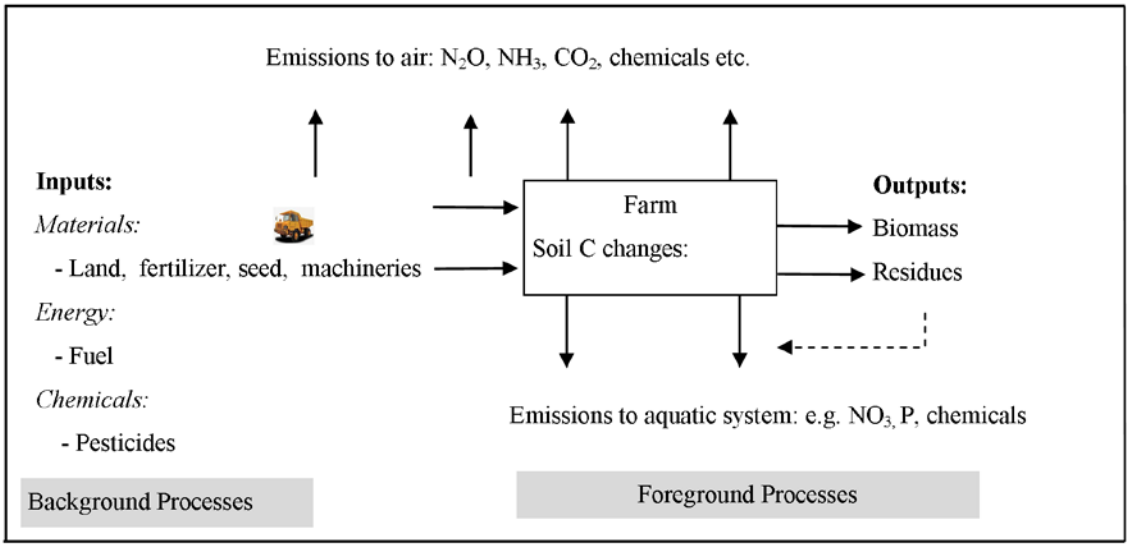

Figure 1: The farm gate system boundary defined for the biomass production

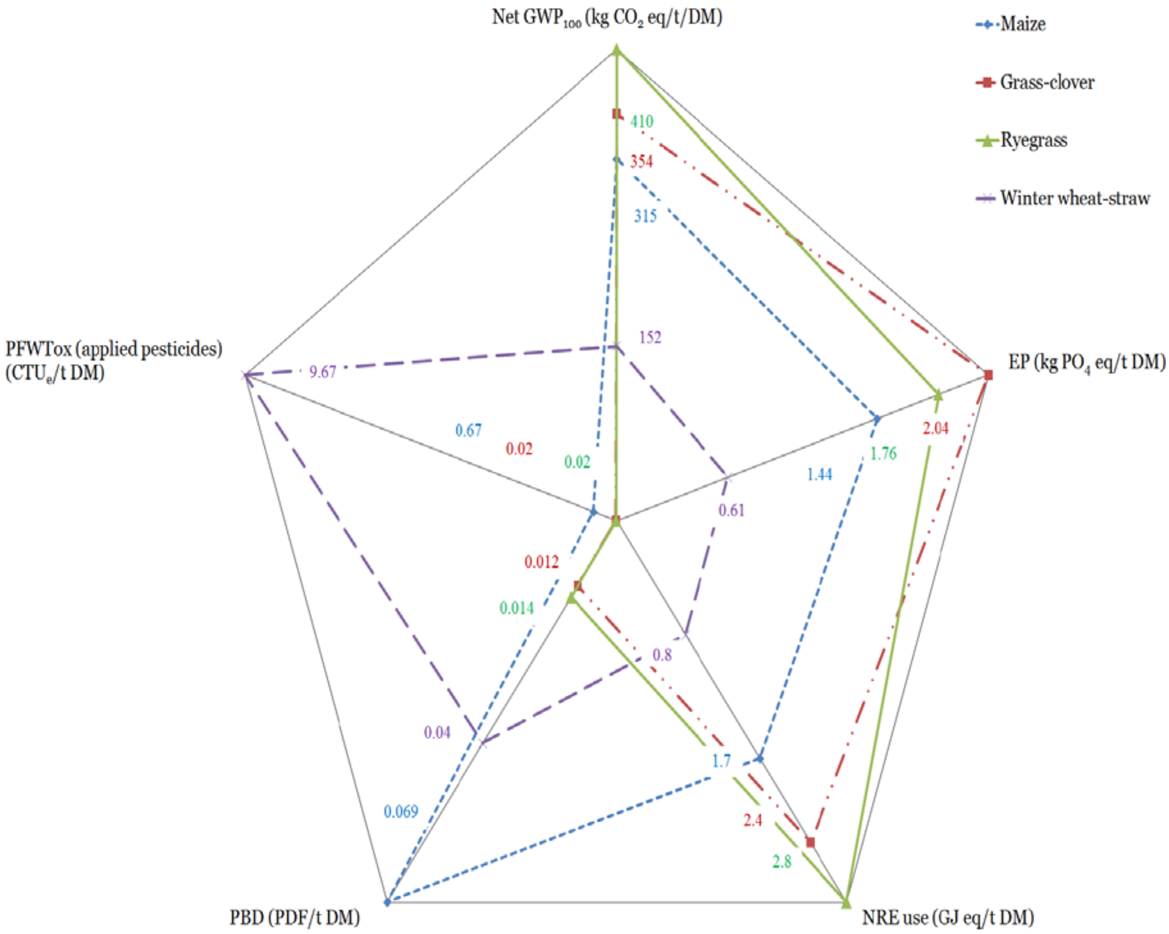

Figure 2: Environmental impact potentials of producing the selected biomass types (GWP_{100} includes soil C change).

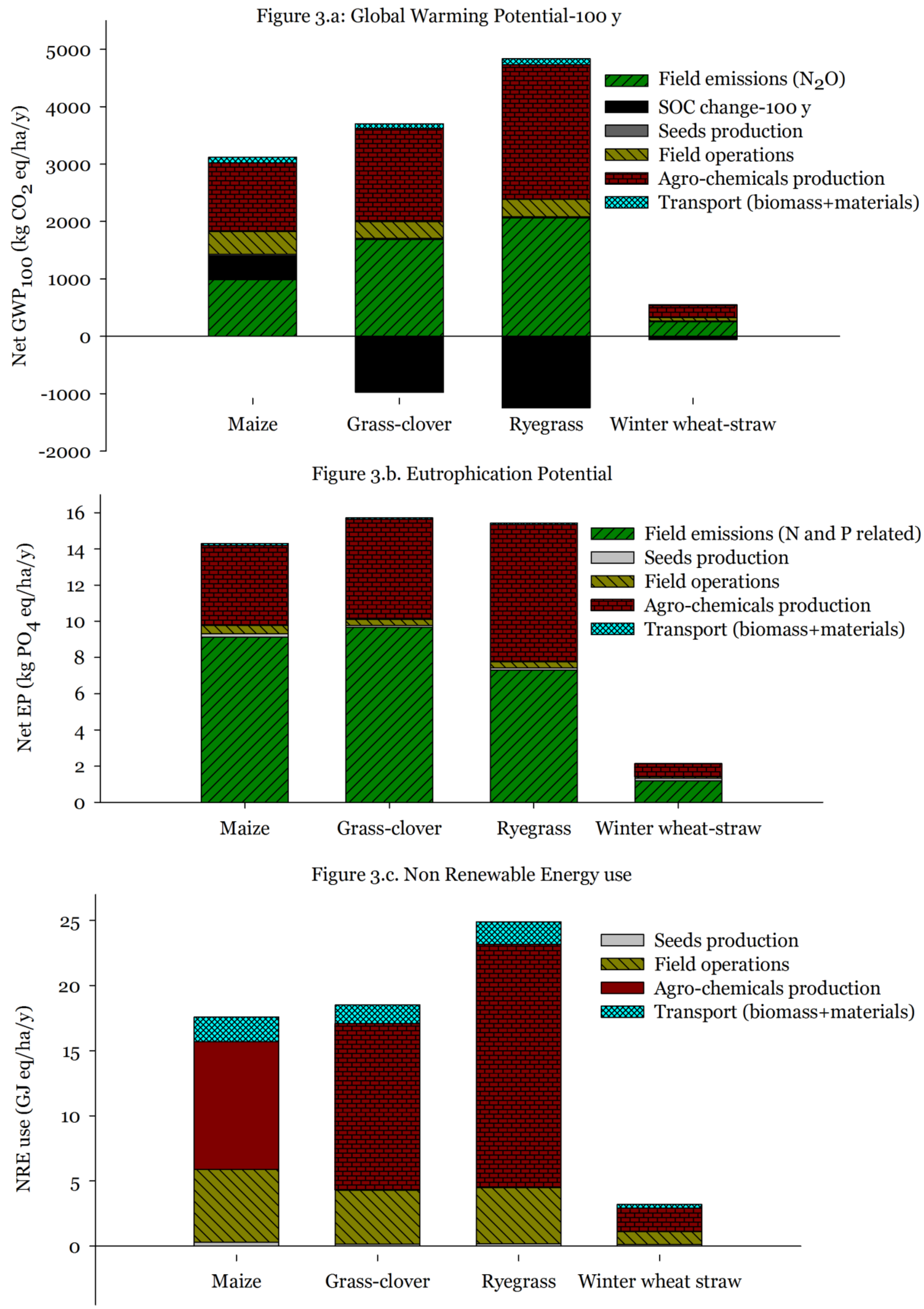

Figure 3: Environmental impact potentials in the related biomass production value chains.

Supporting Information (SI) for simulating the Potential Freshwater Ecotoxicity

Environmental life cycle assessments of producing maize, ryegrass-clover, ryegrass and winter wheat straw for biorefinery

Ranjan Parajuli[a,*], Ib Sillebak Kristensen[a], Marie Trydeman Knudsen[a], Lisbeth Mogensen[a], Andrea Corona[b], Morten Birkved[b], Nancy Peña[c], Morten Graversgaard[a], Tommy Dalgaard[a]

[a]Department of Agroecology, Aarhus University, Blichers Allé 20, 8830-DK, Tjele, Denmark

[b]Department of Manufacturing Engineering and Management, Technical University of Denmark, Building 424, DK-2800 Lyngby, Denmark

[c] Institute of Environmental Science and Technology, Autonomous University of Barcelona, Carrer de les Columnes-08193 Bellaterra, Barcelona, Spain

*Corresponding author, email: ranjan.parajuli@agro.au.dk, Phone: +4571606831

S1. Methods and tools used for the simulation

The Potential Fresh Water Ecotoxicity (PFWTOx) related to the pesticides emissions at the farm level was calculated by using: (i) PestLCI 2.0.6, an inventory model to simulate the emission distribution fractions in respective compartment of the technosphere (Dijkman et al., 2012) and (ii) USEtox 2.0, a characterization model to derive the characterization factors in comparative toxic units (CTU_e) (Fantke et al., 2015; Rosenbaum et al., 2008). The emission distribution fractions to the respective compartments were latter multiplied with the respective CTU_e. The CTUe is expressed as PAF.m^3.day.kg emitted^{-1}) and were simulated using the model "USEtox2" (Fantke et al., 2015).

S2. Data for pesticides active ingredients

The total amount of active ingredients (a.is) of the pesticides considered in this study (Tables S3-S5) was based on the consultation with the experts and checked with the Danish sales supported by Ørum and Samsøe-Petersen (2014). Month of application of the respective a.is were based on the consultation with experts, and from the review of reports and databases (Bøjer and Rydahl, 2013; Planteværn Online, 2015; SEGES, 2015). Of the total mass of a.is (Table S3-5), the share of herbicides (H) was 87% in maize, 72% in ryegrasses and 64% in winter wheat. Growth regulator (GR) was 16% of the total mass assumed for winter wheat, fungicides (F) contributed with 12%, 2% and 19% in maize, ryegrass and grass-clover, and winter wheat respectively. About 26% of the total mass was contributed by insecticides in ryegrass and grass-clover and 1% in maize and winter wheat. Snail control (S) represented only 0.2% in winter wheat (Ørum and Samsøe-Petersen, 2014). Crop growth stages at the time of application of respective a.is were based on SEGES (2010).

S3. Pest LCI data:

The field parameters that were assumed when simulating the emission distribution fractions in the PestLCI 2.0.6 are shown in Table S1. The "average" soil profile (Dijkman et al., 2012) was assumed. In addition, the "adjustable parameters" (included soil material density, fraction of macropores, soil solid matter and water fractions etc.) were the default values, as indicated in the PestLCI2.0 (Dijkman et al., 2012). It should be noted that the model assumes the agricultural field down to a depth of 1 m into the soil and 100 m up into the air as the part of the technosphere, thus the direct emissions to soil can be excluded (Dijkman et al., 2012; Nordborg et al., 2014). Based on this characteristic, we have considered the depth of drainage as zero in the calculation (Table S1), also argued in the same line in Nordborg et al. (2014). The emission distribution fractions to air (f_a), freshwater (fsw), ground water (f_{gw}) and fractions taken-up by plants (f_{uptake}) are shown in Tables S2-4. In the case of pesticides, not listed in the PestLCI 2.0.6 model (indicated in Tables S3-5), the mixing partners based on SEGES (2010) (as show in Tables S3-5) were assumed as alternative. The emission distribution fractions of the assumed mixing partners were calculated from their average fractions simulated in different field scenarios (e.g. timings of application, stages of crop growth, land slope and methods of spraying) (Birkved, 2015, pers. comm.) (Table S2). Field scenarios were constructed considering the uncertainty related to the emission distribution fraction, as discussed in Nordborg et al. (2014) and Birkved and Hauschild (2006), and elaborated as below.

With regard to the uncertainties related to emission distribution fractions, it was found that fresh water emissions were found dependent on both climatic and soil factors, and with the soil parameters explaining most of the variations (Dijkman et al., 2013). The simulation showed that the slope of land do not have impact on the emission to air (f_a), whereas the emission to water (f_{sw}) would increase by a fixed factor of 6 with slope of 6% compared to 1%. Similar result were discussed in Nordberg (2013). Furthermore, if the slope was increased to 7%, the increment in the emission to water was by a factor of 10 compared to the slope of 1%.

Furthermore, since emissions to air are partially related to the air temperature and thus affects the rate of volatilization (Dijkman et al., 2013). This feature was also explained in a comparison of emission distribution of a.is., applied in a Danish agro-climatic conditions and other countries (Dijkman et al., 2013), which implies that such factor is relevant to consider if toxicity impacts of a specific country have to be compared with others. With regard to the variations of soil profile, it was found that emissions to surface water in a sandy soil with low clay content (>55% sand and <20% clay) can be lower by 3−4 times compared to the soils with clay and sand content >20% and <45%, respectively. This was the case of applying the pesticides (atrazine, glyphosate, and metazachlor) (Nordborg et al., 2014).

Table S1: Field parameters assumed for modelling the PestLCI2.0.6

Parameters	Assumption
Climate[a]	Temperate Maritime –I
Soil selection[b]	Average
Spray equipment[c]	Varied as per the stage of crops (see Tables S2-4)
Field Length (m) * width (m)	100*100
Field slope (%)	1
Drainage fraction[d]	0
Drainage depth (m)[d]	Not applicable
Irrigation	No
Tillage	Conventional
Emission compartments used in the study	Air and surface water
Crop stages	See Tables S3-5

[a] PestLCI 2.0.6, based on the climate types as used in footprint of EU climatic zones (Centofanti et al., 2008).

[b] PestLCI 2.0.6, which is based on SPADE database (European Communities, 2010).

[c] Nomenclature as used in PestLCI 2.0.6. For Winter wheat = Cereal-I: leaf development; Cereal-II: tillering; Cereal-III: stem elongation; and Cereal-IV: booting/senescence. For maize = Maize-I: leaf development; Maize-II: stem elongation; Maize-III: inflorescence emergence/flowering; Maize-IV: stem elongation; Maize-V: development of fruit/ripening. For grass-clover and ryegrass = Grass I: all phases. Growth stages are based on SEGES (2010).

[d] PestLCI2.0.6 is only modelled down to a depth of 1 m (Dijkman et al., 2012).

Table S2: Field scenarios for the uncertainty analysis[a]

Simulation scenarios[b,c]	Maize (slope, method, stage of application, month[d])	Winter wheat (slope, method of application, stage of application, month[d])
Scenario I	See Table S3.	See Table S5.
Scenario-II	Slope 1%, Pest LCI field crops, Maize-II, June	1%, PestLCI field crops, Cereals II, April.
Scenario-III	Slope 1%, Conv. Boom, Maize-I, April	1%, PestLCI field, Conv. Boom; Cereals I, October.

[a] Uncertainties are related to calculate the average emission distribution fraction to air and surface water for the a.is, which were not developed in the PestLCI2.0.6

[b] Uncertainty analysis for other different field parameters is additionally discussed in the text section S3.

[c] In the case of grasses, only one method of application was used in the tool (Dijkman et al., 2012) , thus variations in the months for the respective crops are shown in Table S4.

[d] Months were assumed based on SEGES (2015), Bøjer and Rydahl (2013) and Planteværn Online (2015).

Furthermore, for the months starting from March to November, emission to air and to water were found changing by an average factor of 0.99 and 1.32 respectively, the sensitivity was mainly for the Prosulfocarb (Nordberg, 2013). In the same study, in the case of comparing the results related to the application method (e.g. IMAG conv. Boom cereals and IMAB conv.) (see PestLCI 2.0.6) (Dijkman et al., 2012), there were no significant changes in the emission to air and water. Additionally, for the variations caused by different crop-stage it was found that the emissions to air for prosulfocarb increased by a factor of 2,3,4 in the stages Cereal-II, Cereal-III and Cereal-IV respectively, and the emission fraction to water was changed by a factor of 0.8, 0.6 and 0.5 respectively, compared to the stage Cereal-I (Nordberg, 2013). In the case of maize, compared to the stage “Maize-I”, in the stages “Maize-II”, “Maize-III”, and “Maize-IV”, emission to air and water were changed by similar factors as discussed for cereal (as above) (see Table S1 for the spray equipment’s’ nomenclature). In addition, tillage types and field size (with equal length and width) had no impact on the emission distribution fractions.

Table S3. Emission distribution of the selected pesticides application for maize crop, calculated based on PestLCI2.0.6

Pesticide [a]	Types	CAS	Stage of application[b]	Month [c]	Method of application[d]	Application rate [a] (kg/ha/y)	Emission (kg/ha/y)			
							Air (f_a)	Surface water (f_{sw})	Ground water (f_{gw})	Degradation and uptake (f_{uptake})
Bentazone	H	25057-89-0	Maize I	May*	Soil incorporation	3.86E-02	1.5E-04	2.7E-06	7.8E-04	3.8E-02
Fluroxypyr	H	69377-81-7	Maize I	May*	Conv. Boom	3.95E-02	2.3E-04	1.2E-06	3.7E-05	3.9E-02
Iodosulfuron-methyl-natrium	H	144550-36-7	Maize I	April†	Conv. Boom - bare soil	1.81E-02	7.0E-06	1.5E-06	3.6E-04	1.8E-02
Mesotrione[a,1]	H	104206-82-8	Maize-II	June†	Conv. Boom-cereals	7.71E-02	4.3E-03	4.6E-06	1.3E-03	7.2E-02
Pendimethalin	H	40487-42-1	Maize I	May*	Conv. Boom-bare soil	8.92E-03	1.4E-03	8.5E-08	4.8E-06	7.5E-03
Epoxiconazole	F	133855-98-8	Maize I	April†	Conv. Boom – cereals	6.48E-03	5.8E-07	2.6E-09	1.6E-05	6.5E-03
Pyraclostrobin	F	175013-18-0	Maize I	May†	Conv. Boom	1.85E-02	1.6E-04	1.8E-07	3.3E-04	1.8E-02
Cypermethrin	I	52315-07-8	Maize-II	June†	Conv. Boom	1.87E-03	1.8E-06	2.2E-12	7.6E-10	1.9E-03

[a] Type of active ingredients based on (Ørum and Samsøe-Petersen, 2014). [1]Emission distribution of mesotrione assumed similar to terbuthylazine, as a mixing partner, decided after SEGES (2015).

[b] Stages of application, as in PestLCI 2.0.6, and decided based on season/month of application, for the respective a.is. as suggested in SEGES (2015).

[c] Month of application: *per. comm with Per Kudsk, Lise Nistrup Jørgensen and Poul Henning Petersen (2014).

[d] Method assumed based on scenarios presented in Birkved and Hauschild (2006) and Nordberg (2013).

†for the mixing partner months decided after SEGES (2015), Bøjer and Rydahl (2013) and Planteværn Online (2015).

Table S4. Emission distribution of the selected pesticides application for grass-clover and ryegrass, calculated based on PestLCI2.0.6

Pesticide [a]	Types	CAS	Stage of application [b]	Month[c]	Method of application[d]	Application rate[a] (kg/ha/y)	Emission (kg/ha/yr)			
							Air (f_a)	Surface water (f_{sw})	Ground water (f_{gw})	Degradation and uptake (f_{uptake})
Bentazone	H	25057-89-0	Grass I	May*	Conv. Boom-bare soil	8.0E-03	1.9-04	4.5E-07	1.3E-04	7.7E-03
Fluroxypyr	H	69377-81-7	Grass I	May*	Field crops	2.1E-06	5.4E-08	4.9E-11	1.6E-09	2.0E-06
MCPA	H	94-74-6	Grass I	April	Field crops	1.2E-02	1.6E-03	1.6E-07	1.9E-05	1.0E-02
Phenmedipham†	H	13684-63-4	Grass I	May	Field crops	1.6E-03	1.3E-05	2.6E-09	1.7E-07	1.5E-03
Propiconazole	F	60207-90-1	Grass I	March	Field crops	5.0E-04	1.4E-04	0.0E+00	1.6E-06	3.6E-04
Dimethoate	I	60-51-5	Grass I	May	Field crops	7.8E-03	2.6E-04	1.2E-07	1.4E-05	7.5E-03

[a] Type and doze of active ingredients based on (Ørum and Samsøe-Petersen, 2014). †Includes the mass of thifensulfuron- methyl also.

[b] Stages of application, as in PestLCI 2.0.6, and decided based on season/month of application, for the respective a.is. as suggested in SEGES (2015).

[c] Month of application is based on: *per. comm with Per Kudsk, Lise Nistrup Jørgensen and Poul Henning Petersen (2014); and †similar to the mixing partners (SEGES, 2015) and based on: Bøjer and Rydahl (2013), Brüsch et al. (2015) and Planteværn Online (2015).

[d] Method assumed based on scenarios presented in Birkved and Hauschild (2006) and Nordberg (2013).

Table S5. Emission distribution of the selected pesticides application for winter-wheat, calculated based on PestLCI2.0.6 (H = herbicides; I = insecticides; F= fungicides; GR= growth regulator and S= snails stop)

Pesticide [a]	Types	CAS	Stage of application [b]	Month [c]	Method of application[d]	Application rate[a] (kg/ha/y)	Emission (kg/ha/yr)			
							Air (f_a)	Surface water (f_{sw})	Ground water (f_{gw})	Degradation and uptake (f_{uptake})
2,4-d[a,1]	H	94-75-7	Cereals II	April	Conv.boom-cereals	8.4E-03	3.0E-04	7.9E-08	1.5E-05	8.1E-03
Bromoxynil	H	1689-84-5	Cereals II	April*	Conv.boom-cereals	1.6E-02	2.5E-03	8.4E-10	2.2E-06	1.4E-02
	H	1689-84-5	Cereals I	Oct*	Conv.boom-cereals	1.6E-02	9.5E-04	6.7E-09	4.7E-06	1.5E-02
Clodinafop-propargyl	H	105512-06-9	Cereals III	May†	Conv.boom-cereals	4.8E-04	4.9E-06	5.9E-10	2.1E-07	4.7E-04
Diflufenican [a,2]	H	83164-33-4	Cereals I	October*	Conv.boom-cereals	2.5E-02	1.9E-04	1.6E-07	6.2E-06	2.5E-02
Fenoxaprop-p-ethyl	H	71283-80-2	Cereals III	May	Conv.boom-cereals	1.6E-03	3.7E-06	6.9E-11	1.9E-08	1.6E-03
Florasulam	H	145701-23-1	Cereals II	April†	Conv.boom-cereals	1.1E-03	5.5E-04	3.1E-10	2.6E-08	5.5E-04
Fluroxypyr	H	69377-81-7	Cereals II	May*	Conv.boom-cereals	2.8E-02	1.6E-04	3.3E-07	1.0E-05	2.8E-02
Iodosulfuron-	H	144550-36-7	Cereals II	April	Conv.boom-	1.3E-03	7.3E-07	4.9E-09	5.5E-06	1.3E-03

methyl-natrium					cereals					
Ioxynil	H	1689-83-4	Cereals II	October	Conv.boom-cereals	3.0E-02	3.2E-05	1.5E-07	1.4E-05	3.0E-02
MCPA	H	94-74-6	Cereals III	May*	Conv.boom-cereals	1.5E-01	3.9E-03	2.1E-05	5.3E-04	1.4E-01
Mesosulfuron	H	400852-66-6	Cereals II	April†	Conv.boom-cereals	8.0E-04	1.1E-07	6.3E-10	9.0E-07	8.0E-04
Metsulfuron-methyl	H	74223-64-6	Cereals II	April*	Conv.boom-cereals	5.1E-04	7.1E-08	9.5E-11	5.7E-07	5.1E-04
Pendimethalin	H	40487-42-1	Cereals I	Oct*	Conv.boom-cereals	1.2E-01	8.5E-03	4.3E-07	3.1E-05	1.1E-01
Prosulfocarb [a,3]	H	52888-80-9	Cereals I	October*	Conv.boom-cereals	6.9E-01	4.6E-03	6.2E-07	4.1E-05	6.9E-01
Sulfosulfuron	H	141776-32-1	Cereals II	April†	Conv.boom-cereals	2.4E-04	2.4E-06	2.6E-09	1.1E-07	2.4E-04
Tribenuron-methyl[a,4]	H	101200-48-0	Cereals II	April	Conv.boom-cereals	1.2E-03	8.0E-06	1.7E-07	4.2E-06	1.2E-03
Chlormequat-chloride [a,5]	GR	999-81-5	Cereals III	June	Conv.boom-cereals	2.6E-01	1.3E-04	2.1E-06	1.4E-04	2.6E-01
Ethephon	GR	16672-87-0	Cereals III	June	Conv.boom-cereals	8.2E-03	6.5E-03	1.4E-07	2.0E-06	1.6E-03
Mepiquat-chloride	GR	24307-26-4	Cereals III	June	Conv.boom-cereals	3.6E-03	1.8E-06	1.4E-09	7.8E-08	3.6E-03

Trinexapac-ethyl	GR	95266-40-3	Cereals III	June	Conv.boom-cereals	4.1E-03	2.8E-03	1.3E-11	1.4E-10	1.3E-03
Azoxystrobin[a,]	F	131860-33-8	Cereals I	May	Conv.boom-cereals	7.1E-04	4.6E-06	1.3E-08	1.1E-07	7.0E-04
Boscalid	F	188425-85-6	Cereals II	May[†]	Conv.boom-cereals	7.5E-02	5.2E-04	1.2E-07	3.9E-04	7.4E-02
Cyprodinil[a,6]	F	121552-61-2	Cereals III	June	Conv.boom-cereals	9.1E-04	3.7E-04	6.6E-11	1.6E-08	5.3E-04
Difenoconazole	F	119446-68-3	Cereals IV	May[†]	Conv.boom-cereals	5.9E-04	1.5E-05	9.0E-10	6.6E-08	5.7E-04
Epoxiconazole[a,7]	F	133855-98-8	Cereals III	May*,[†]	Conv.boom-cereals	1.0E-01	5.7E-04	5.7E-04	5.2E-04	9.9E-02
Fludioxonil	F	131341-86-1	Cererals III	May[†]	Conv.boom-cereals	2.5E-03	2.5E-05	3.0E-08	3.3E-07	2.5E-03
Imazalil	F	35554-44-0	Cereals III	May[†]	Conv.boom-cereals	2.7E-03	1.9E-05	6.3E-09	3.3E-07	2.7E-03
Metconazole	F	125116-23-6	Cereals III	May[†]	Conv.boom-cereals	1.6E-05	5.6E-06	1.8E-13	1.5E-10	8.5E-06
Metrafenone	F	220899-03-6	Cereals III	May[†]	Conv.boom-cereals	1.5E-02	9.1E-03	8.0E-09	1.0E-06	8.3E-03
Propiconazole	F	60207-90-1	Cereals III	May*	Conv.boom-cereals	1.4E-02	3.0E-04	0.0E+00	4.7E-05	1.3E-02
Prothioconazole	F	178928-70-6	Cereals III	May[†]	Conv.boom-cereals	5.1E-02	1.7E-04	7.9E-08	5.8E-06	5.1E-02

Prothioconazole	F	178928-70-6	Cereals IV	June†	Conv.boom-cereals	4.2E-03	1.0E-05	4.9E-09	1.9E-07	4.1E-03
Pyraclostrobin	F	175013-18-0	Cereals III	May*†	Conv.boom-cereals	3.0E-02	1.4E-02	2.3E-09	7.4E-07	1.6E-02
Tebuconazole	F	107534-96-3	Cereals IV	May*	Conv.boom-cereals	2.5E-02	2.8E-05	5.7E-08	3.0E-06	2.5E-02
Thiabendazole	F	148-79-8	Cereals IV	May†	Conv.boom-cereals	5.2E-04	3.9E-06	1.8E-09	6.8E-08	5.1E-04
Alpha-cypermethrin[a,8]	I	67375-30-8	Cereals IV	June	Conv.boom-cereals	2.5E-03	3.9E-06	1.6E-11	6.5E-09	2.5E-03
Cypermethrin	I	52315-07-8	Cereals IV	June	Conv.boom-cereals	4.4E-03	2.6E-06	1.7E-12	5.9E-10	4.4E-03
Lambda-cyhalothrin	I	91465-08-6	Cereals IV	June*	Conv.boom-cereals	1.5E-04	1.6E-05	3.9E-13	2.0E-11	1.4E-04
Pirimicarb	I	23103-98-2	Cereals IV	June	Conv.boom-cereals	2.6E-03	5.9E-04	4.0E-09	2.7E-07	2.0E-03
Tau-fluvalinate	I	102851-06-9	Cereals IV	June	Conv.boom-cereals	1.2E-02	1.7E-06	2.6E-11	1.0E-08	1.2E-02
Ferrifosfat[a,9]	S	10045-86-0	Cereals III	June†	Conv.boom-cereals	3.4E-03	5.4E-04	1.4E-07	2.5E-06	2.9E-03
Ferrifosfat[a,9]	S	10045-86-0	Cereals II	April†	Conv.boom-cereals	2.9E-04	2.3E-04	8.7E-09	1.1E-07	5.9E-05

[a] Type of active ingredients based on (Ørum and Samsøe-Petersen, 2014). The a.i included the mass of: [1]aminopyralid; [2]flupyrsulfuron-methyl; [3]pyroxsulam; [4]thifensulfuron-methyl and picolinafen; [5]prohexadion-calcium; [6]picoxystrobin; [7]fenpropidin; [8]gamma-cyhalothrin, [9]assumed as carbofuran, due to data unavailability and are decided based on the respective mixing partners (SEGES, 2015).

[b] Stages of application, as in PestLCI 2.0.6, and decided based on the month of application assumed for the respective a.is.

[c] Month of application is based on: *per. comm with Per Kudsk, Lise Nistrup Jørgensen and Poul Henning Petersen (2014). See section S3.

[d] Application method assumed based on scenarios presented in Birkved and Hauschild (2006) and Nordberg (2013).

[†]Emission distribution fraction assumed after the average of the mixing partners (SEGES, 2015) and based on: Bøjer and Rydahl (2013) and Planteværn Online (2015), and thus accordingly the month of application.

S4. Characterization factors for freshwater ecotoxicity

In our study the characterization factors, expressed as CTUe per kg emission are calculated at midpoint level (Table S6). The methods on how to apply the model are elaborated on Fantke et al. (2015). In the case of mesotrione, which were not in the USEtox 2.0 it was calculated based on the recommended procedure (Fantke et al., 2015). The physio-chemical and ecotoxic effect data (Table S7) required by the USEtox model are adapted from the sources e.g. Footprint PPDB (2011) and EPA (2015a). The required physio-chemical data were also derived from the Estimation Program Interface Suite$_{TM}$ (EPISuite) for Windows v. 4.11 (EPA, 2015b) and in accordance to as suggested in Nordborg et al. (2014). Due to the lack of characterization factor for the Ferrifosfat the comparative toxicity potential for Fe(III) (SEGES, 2015) was assumed. This because that the toxicity potential for inorganic pesticides depend mainly by the interactions of the ions of the heavy metal (in this case Fe(III) presented in the chemical compound with the surrounding environment and the targeted pests (Dong et al., 2014).

S5. Calculation of the PFWTox

PFWTox, is calculated as in equation-i, where M_i represents the mass emitted in the compartment *i* (emission distributions for different scenarios Tables S3-5) and CF_{ti} as the related toxicity characterization factor, and summed over all emission compartments *i* (Nordborg et al., 2014; Rosenbaum et al., 2008).

$$IS_t = \sum_i (CF_{ti} \times M_i)$$

.........equation i

In the case of wheat the higher impact are partly because of the following reasons: (i) for the common types of a.is, applied in the both crops (e.g. fluroxypyr, iodosulfuron, pendimethalin, epoxiconazole, pyraclostrobin and cypermethrin), the CTU_e/ha/y was collectively higher by two-fold in winter wheat compared to maize (SI Tables S3-S6). (ii) in addition to the common types of a.is, additional a.is considered in winter wheat contributed significantly to the impact (see SI, Table S5); (iii) the total a.is per ha in winter wheat is higher than maize, and 40% of it is covered by the herbicide (Prosulfocarb). Despite the CTUe per kg emission of prosulfocarb is only 1.46, the emission distribution fractions of it to air and freshwater is higher, (iv) consideration of mesotrione in the maize crop also has significantly lower CTUe per kg emissions (SI Table S6), which makes the crop with lower ecotoxicity effect.

Table S6. Characterization factors to calculate PFWTox, based on USEtox 2.0 model

Pesticides, a.i.	$CTU_e\ kg^{-1}$ emission	
	airC	fr.waterC
2,4-d	3E+01	9E+02
Alpha-cypermethrin	3E+05	3E+07
Azoxystrobin	1E+04	8E+04
Bentazone	3E+00	2E+02
Boscalid[1]	4E+02	1E+04
Bromoxynil	7E+02	2E+04
Chlormequat-chloride	2E+01	2E+02
Clodinafop-propargyl	3E+02	3E+04
Cypermethrin	5E+05	5E+07
Cyprodinil	7E+01	3E+04
Difenoconazole	4E+03	1E+05
Diflufenican	5E+01	2E+03
Dimethoate	2E+02	2E+04
Epoxiconazole[1]	2E+03	1E+05
Ethephon	1E+02	1E+03
Fenoxaprop-p-ethyl	5E+02	6E+04
Ferrifosfat[2]	7E+04	2E+05
Fludioxonil	8E+02	1E+05
Florasulam	2E+03	1E+04
Fluroxypyr	1E+02	3E+03
Imazalil	9E+01	2E+04
Iodosulfuron-methyl-natrium[1]	2E+03	1E+04
Ioxynil	7E+02	2E+04
Lambda-cyhalothrin	8E+05	1E+08
MCPA	2E+01	9E+01
Mepiquat-chloride	1E+01	8E+02
Mesotrione[3]	3E+01	8E+02
Metconazole[1]	3E+02	2E+04
Metrafenone[1]	7E+01	3E+04
Metsulfuron-methyl	1E+03	2E+04
Pendimethalin	3E+03	4E+05
Phenmedipham	8E+02	4E+04
Pirimicarb	8E+00	2E+03
Propiconazole	4E+02	2E+04

Prosulfocarb	3E+02	3E+04
Prothioconazole[1]	3E+03	7E+04
Prothioconazole[1]	3E+03	7E+04
Pyraclostrobin[1]	2E+03	5E+05
Sulfosulfuron	1E+02	5E+03
Tau-fluvalinate	5E+03	8E+05
Tebuconazole	2E+03	7E+04
Thiabendazole	8E+02	3E+04
Tribenuron-methyl	3E+01	7E+02
Trinexapac-ethyl	4E+00	1E+03

[1] CTUe are adapted from Nordborg et al. (2014).

[2] Characterization factors of Jern III (SEGES, 2015) are assumed.

[3] CTUe, calculated and parameters are shown in Table S7.

Table S7. Principal physico-chemical data used in USEtox 2.0

Parameter	Units	Mesotrione Values
Molecular weight (MW)[1]	(g mol-1)	3,39E+02
Dissociation constant (pKa)	-	3,12E+00
Octanol-water partition coefficient (Kwo) [1]	Log P	1,10E-01
Henry law coefficient (at 25°C)	Pa.m3.mol-1	1,23E-05
Vapour pressure (at 25°C)	Pa	5,70E-06
Solubility - In water (at 25°C)	mg.L-1	1,58E+02
Degration rate in air	s-1	1,09E-05
Degration rate in water	s-1	1,34E-07
Degration rate in sediment	s-1	1,49E-08
Degration rate in soil	s-1	6,97E-07
species-specific eco-toxicity data[2]	log(mg.L-1)	1,54E+00
Bioaccumulation factor in fish	L.kgfish-1	2,33E+00

[1](Footprint PPDB, 2011)

[2] Average of the log-values of the species-specific eco-toxicity data , after Payet (2004) .

Reference List

Birkved, M., Hauschild, M.Z., 2006. PestLCI - A model for estimating field emissions of pesticides in agricultural LCA. Ecological Modelling 198, 433-451.

Bøjer, O., Rydahl, P., 2013. Dokumentation for ukrudtsmodulet i Planteværn Online (in Danish). Aarhus University, Science and Technology. 97.https://plantevaernonline.dlbr.dk/cp/documents/Infoweeds.pdf (accessed Oct 22, 2015).

Brüsch, W., Rosenbom, A.E., Badawi, N., Gudmundsson, L., 2015. The Danish Pesticide Leaching Assessment Programme: Monitoring results May 1999–June 2013 Copenhagen K, Denmark 159.http://pesticidvarsling.dk/xpdf/vap-results-99-13.pdf (accessed Oct 22, 2015).

Centofanti, T., Hollis, J.M., Blenkinsop, S., Fowler, H.J., Truckell, I., Dubus, I.G., Reichenberger, S., 2008. Development of agro-environmental scenarios to support pesticide risk assessment in Europe. Science of The Total Environment 407, 574-588.

Dijkman, T.J., Birkved, M., Hauschild, M.Z., 2012. PestLCI 2.0: a second generation model for estimating emissions of pesticides from arable land in LCA. International Journal of Life Cycle Assessment 17, 973-986.

Dijkman, T.J., Birkved, M., Hauschild, M.Z., 2013. Modelling of pesticide emissions for Life Cycle Inventory analysis: model develop-ment, applications and implications. Copenhagen, Denmark. 96.http://orbit.dtu.dk/files/96859233/Modelling_of_pesticide_emissions.pdf (accessed Jan 12, 2016).

Dong, Y., Gandhi, N., Hauschild, M.Z., 2014. Development of Comparative Toxicity Potentials of 14 cationic metals in freshwater. Chemosphere 112, 26-33.

EPA, 2015a. ECOTOX Database.Environment Protection Agency.http://cfpub.epa.gov/ecotox/quick_query.htm (accessed Dec 22, 2015).

EPA, 2015b. Estimation Programs Interface EPISuiteTM.http://www.epa.gov/tsca-screening-tools (accessed Dec 22, 2015).

European Communities, 2010. Land management and natural hazards unit: Soil profile data.http://eusoils.jrc.ec.europa.eu/projects/spade/ (accessed Sep 14, 2015)

Fantke, P.E., Huijbregts, M., Margni, M., Hauschild, M., Jolliet, O., McKone, T., Rosenbaum, R., Meent, D.v.d., 2015. USEtox® 2.0 User Manual (Version 2). UNEP/SETAC scientific consensus model for characterizing human toxicological and ecotoxicological impacts of chemical emissions in life cycle assessment.http://usetox.org (accessed Nov 15, 2015).

Footprint PPDB, 2011. The footprint pesticide properties database. Agriculture and Environmental Research unit (AERU), University of Hertfordshire, page cited 28 April 2011.http://sitem.herts.ac.uk/aeru/ppdb/en/Reports/442.htm (accessed Dec 22, 2015).

Nordberg, M., 2013. Pesticide use and freshwater ecotoxic impacts in biofuel feedstock production: a comparison between maize, rapeseed, Salix, soybean, sugarcane and wheat. Department of Energy and Environment Master of Science Thesis in Industrial Ecology

Göteborg, Sweden.
183.http://publications.lib.chalmers.se/records/fulltext/206817/206817.pdf.
Nordborg, M., Cederberg, C., Berndes, G., 2014. Modeling Potential Freshwater Ecotoxicity Impacts Due to Pesticide Use in Biofuel Feedstock Production: The Cases of Maize, Rapeseed, Salix, Soybean, Sugar Cane, and Wheat. Environmental Science & Technology 48, 11379-11388.
Ørum, J.E., Samsøe-Petersen, L., 2014. Bekæmpelsesmiddelstatistik 2013: behandlingshyppighed og belastning. 66.http://www2.mst.dk/Udgiv/publikationer/2014/12/978-87-93283-33-6.pdf (accessed Dec 15, 2015).
Payet, J., 2004. Assessing toxic impacts on aquatic ecosystems in life cycle assessment (LCA).
Planteværn Online, 2015. Agro-region: Denmark Strategy for a growing season.http://www.ipmdss.dk/cp/SeasonPlan/Plan.asp?id=djf&ProblemGroupID=50&language=da (accessed Oct 22, 2015)
Rosenbaum, R., Bachmann, T., Gold, L., Huijbregts, M.J., Jolliet, O., Juraske, R., Koehler, A., Larsen, H., MacLeod, M., Margni, M., McKone, T., Payet, J., Schuhmacher, M., van de Meent, D., Hauschild, M., 2008. USEtox—the UNEP-SETAC toxicity model: recommended characterisation factors for human toxicity and freshwater ecotoxicity in life cycle impact assessment. Int J LCA 13, 532-546.
SEGES, 2010. Growing instructions-Crops.https://dyrk-plant.dlbr.dk/Web/(S(pgsviibw4c1053wjgai5ni1p))/forms/Afgroeder.aspx?kategori=1 (accessed Sep 12, 2015).
SEGES, 2015. Middeldatabasen.Aarhus, Denmark.https://www.middeldatabasen.dk/ (accessed Nov 09, 2015).